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CONTENTS

		PAGE
71.	On some biochemical properties of natural coumarins.—By Dr. P. K. Bose ...	367
72.	A study of the carbylamine reaction.—By Sameer Bose	376
73.	A study in the complex formation of beryllium ions with hydroxy-carboxylic acids.—By I. D. Varma and R. C. Mehrotra	381
74.	Synthesis of 5-methoxy-2-indanone.—By Amareshwar Chatterjee, Ramesh Chandra Chatterjee and Bidyut Kamal Bhattacharyya	391
75.	A study of the hydrogen bonding in *o*-nitrophenol in presence of *p*-nitrophenol.—By S. M. Deshpande and N. V. Parthasarathy	399
76.	Thiazole derivatives as antispasmodics and antihistaminics. Part III.—By Pranabandhu Tripathy, H. K. Pujari and M. K. Rout	407
77.	Action of nitrogen dioxide and its dissociation products on nitrites of sodium, potassium and silver.—By Vasantrai Trambaklal Oza	411
78.	Amino derivatives of titanium tetrabromide. Part IV.—By Sarju Prasad and Jai Beniprasad Tripathi	415
79.	Some aliphatic moncarboxylate complexes of bivalent metals in aqueous solution. Part VII. Manganese acetato complexes.—By S. K. Siddhanta and S. N. Banerjee	419
80.	Some aliphatic monocarboxylate complexes of bivalent metals in aqueous solution. Part VIII. Nickel mono-acetato complex.—By S. K. Siddhanta and S. N. Banerjee	423
81.	Some aliphatic monocarboxylate complexes of bivalent metals in aqueous solution. Part IX. Nickel acetato complexes.—By S. K. Siddhanta and S. N. Banerjee	426
82.	Rubeanic acid and its derivatives as colorimetric reagents. Part I. Spectrophotometric determination of cobalt, nickel, palladium, silver and ruthenium with rubeanic acid.—By J. Xavier and Priyadaranjan Rây	432
83.	Formation of aluminium *o*-cresotate chelate: Potentiometric and conductometric studies.—By S. C. Tripathi and Satya Prakash	445
84.	Ion-activity measurement with resin-membrane electrodes: Measurement of zinc, cadmium and manganese ion-activity in electrolytic solutions.—By A. S. Basu	451
Short Notes:		
10.	Volumetric method for the determination of small amounts of silver in presence of large amounts of copper and nickel.—By K. C. Seal	453
11.	Attempts on the synthesis of coniferin.—By Durgeshwari Prasad and D. N. Chaudhury	455

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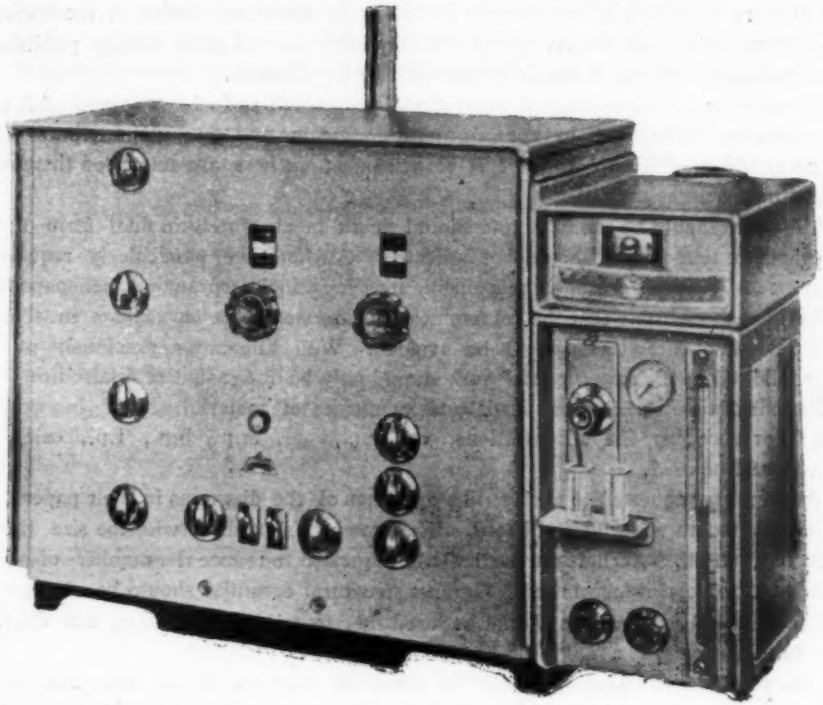

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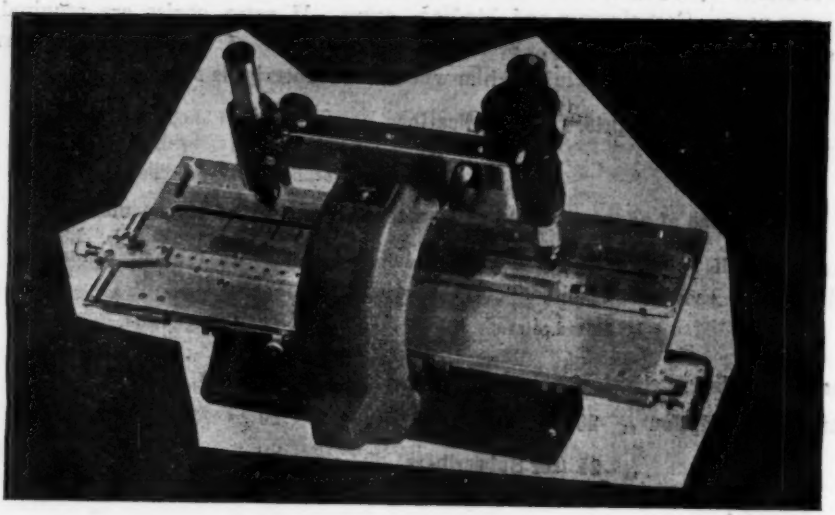

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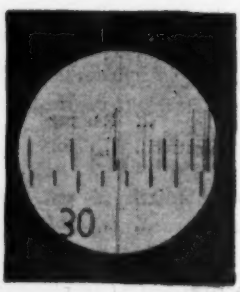

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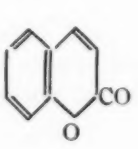
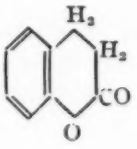
ON SOME BIOCHEMICAL PROPERTIES OF NATURAL COUMARINS*

By Dr. P. K. Bose, D.Sc., F.N.I.

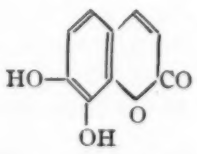
Natural coumarins occupy an important place among plant constituents. Coumarin (I), the simplest member of the series, was isolated from tonka bean (*Dipteryx odorata* Willd.) by Vogel[1] in 1820 and immediately attracted the attention of perfumers on account of its pleasant and persistent odour. Coumarin has since been located in more than 80 different plants. Dihydrocoumarin (II) has a similar odour and some methoxy- and hydroxy-coumarins have also this characteristic, though not pronounced. More complex coumarins are practically odourless at the ordinary temperature. A systematic correlation between aroma and chemical constitution in the coumarin series is lacking, though the odour seems to be associated with the lactonic structure and presence of a 3 : 4-double bond.



Coumarin (I)



Dihydrocoumarin (II)



Daphnetin (III)

Many natural coumarins affect the living cells of plants and animals in various ways. The influence of coumarins in bringing about biochemical changes is being gradually recognized in many fields of study. Most of the work has been done with the parent member of the group, namely coumarin, and many interesting results have been recorded.

Coumarin itself, which is a fairly common plant metabolite, inhibits the germination and subsequent root-growth of plants. Klebs[2] observed its toxic action on algae, while Shreiner, Reed and Skinner[3] recorded its inhibitory effects on the growth of wheat. Cameron[4] reported that daphnetin (III), another member of this group, behaved in the same way. Sigmund[5] noted the effects of both daphnetin and its isomer, æsculetin, on seed germination. It has since been shown that a number of unsaturated lactones including coumarin possess what is called the "blastocholine" effect, *i.e.*, the property to suppress the germination of seeds[6], at low concentrations.

* Presidential address delivered at the Annual General Meeting of the Society in Madras on January 8, 1958.

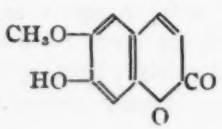
The phytocidal action of coumarin was also studied by Audus and Quastel[7], who observed that coumarin exerted a marked inhibition of both germination and root-growth, the latter being more susceptible than germination. Further, its action is a differential one, carrot, for example, being 20 times as sensitive as cress. The formative effects on the hypocotyl are also marked. The inhibitory effects of coumarin, being reversible, are supposed to arise from loose combinations or easily dissociated compounds of coumarin with enzymes or metabolites of the plant cell. It is now believed that enzymes are inactivated by addition of the sulphydryl groups to the 3:4 double-bond of coumarin. Thiourea lifts this inhibition.

Coumarin also reduces the germination of the eyes of potato tubers[8], but the rate of germination of barley grains is increased by their immersion in coumarin solution (10^{-7} to $10^{-10}M$) for 24 hours. It has thus an activity like that of indole-3-acetic acid. The root-growth of tomato is inhibited by a concentration of 0.05 mg./100 c.c., but is stimulated at a higher dilution[9] of 0.0001-0.0005 mg./100 c.c.—an interesting observation.

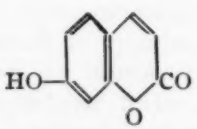
The inhibiting activity of a number of coumarins is shown in Table I (F. Moewus, *Naturforsch. u. Med. in Deutschland*, 1939-46, Band 40, Biochem. Teil II, p. 185).

There is also a good probability that coumarins act as growth regulators in a number of plants. This is supported by the fact that the plant, *Melilotus officinalis*, in which coumarin normally occurs, is not capable of thriving when made coumarin-free by proper breeding[10].

Tobacco plants infected with tomato wilt virus, and virus-infected tubers and oat roots have been found to contain scopoletin (IV).



Scopoletin (IV)



Umbelliferone (V)

Roots having the highest concentration of scopoletin showed the slowest growth[11]. Both umbelliferone (V) and scopoletin are produced in the sound (uninjured) part of the injured sweet potato. These inhibit the growth of *Ceratostomella fimbriata*, a fungus, in dilutions of 1:1000 and 1:4000 respectively. Appearance, under ultraviolet light, of blue fluorescence can be used to distinguish healthy from injured sweet potato affected by this fungus and many other pathogens[12].

The blastocholine action of coumarins is not confined to plants. Grimm[13] observed that tadpoles of *Xenopus levis* brought into solutions of coumarin (1:10^6 to $1:4\times10^6$) for 10-20 days after hatching developed into frogs inferior in weight as

compared to controls. Further, coumarin (1 in 2500) and æsculetin (1 in 5000) could arrest or retard the growth of *Rana esculenta* at the larval stage. It would be quite interesting to see how the youngs of other animals behave towards these and allied substances.

TABLE I

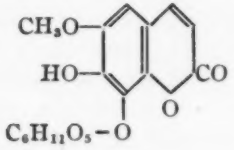
Inhibiting effect of different coumarins.

Coumarin.	*Conc.*	*% Germination.*	*% Inhibition.*
Ayapin	$1:10^6$	87	19
Bergapten	$1:10^6$	83	15
Pimpinellin	$1:10^6$	73	23
Seselin	$1:10^6$	59	30
Daphnetin	$1:2\ 10^6$	80	29
Xanthotoxin	$1:5.10^5$	77	59
Xanthotoxin	$1:5.10^6$	63	34
Nodakenin (glucoside)	$1:2.10^4$	93	9
Nodakenin (glucoside)	$1:10^5$	89	0
Nodakenetin	$1:2.10^4$	83	35
Nodakenetin	$1:10^5$	87	12
Skimmin (glucoside)	$1:2.10^4$	93	30
Skimmin (glucoside)	$1:10^5$	92	5
Umbelliferone (aglycone)	$1:2.10^4$	97	60
Umbelliferone (aglycone)	$1:4.10^4$	88	50
Umbelliferone (aglycone)	$1:8.10^4$	91	37
Umbelliferone (aglycone)	$1:10^5$	88	19
Cichoriin (glycoside)	$1:2.10^4$	93	+5
Æsculetin (aglycone)	$1:2.10^4$	91	+5

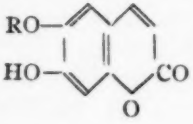
Coumarin has interesting cytogenetic properties. A technique of chromosome analysis with the help of coumarin has been developed by Sharma and Bal[14] and good results have been obtained. Pre-treatment in coumarin for short periods results in satisfactory clarification of plant chromosomes, but prolonged treatment causes fragmentation, and chromosomes become pycnotic. Cyto-histological and macroscopical effects of coumarin and its derivatives have been studied by Quercioli[15] in *Allium cepa*. Pre-prophasic inhibition, stickiness, mutagenic action, C-mitotic effects etc. are produced with mutagenic concentrations of these chemicals. It has been suggested that coumarins attack mainly interkinetic chromosomes while the mutagenic action of other compounds concerns the mitotic chromosomes. The substances studied include the acetyl derivatives of umbelliferone and æsculetin, which also exhibit root-inducing effect.

Coumarins behave differently towards animals. de Moura Campos[16] noticed a true curare-like action of coumarin, while Marolda[17] observed a diminution of tone and decrease or suppression of peristalsis on subjecting isolated strips of rabbit's small intestine to increasing concentrations of coumarin.

Coumarin acts as a narcotic for some animals (*e.g.* rabbit, earthworm) and as a sedative and hypnotic for mice. Some larger animals, such as sheep, dogs and horses, can be killed by coumarin, the lethal doses being 5 g., 0.6-0.8 g. and 40 g. respectively[18]. Moderate quantities have no marked effect on human subjects except its curare-like action. Fraxin (VI) causes paralysis of the central nervous system of frogs and mice on intravenous injection[19].



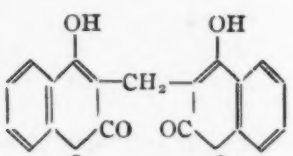
Fraxin (VI)



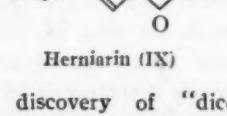
[Æsculin : R = $C_6H_{11}O_5$ (VII)
Æsculetin : R = H]

Both urine volume and uric acid elimination in rabbits are increased by administration of fraxin. Fraxin caused increase in urine volume to 1.6 times per hour on an average for 8 hours. During this period, the uric acid in urine increased to 2.1 times the normal. It has therefore been found to be superior to "atophan" in the treatment of gout[20].

Some simpler coumarin derivatives have pronounced activity like that of vitamin P. The capillary resistance of normal guinea-pigs is raised and the capillary fragility of scorbutic guinea-pigs is decreased by injections of æsculin (VII). Ingestion of 20 mg. of the substance by human subjects increases capillary resistance and the effect persists for more than a week[21].



Dicoumarol (VIII)



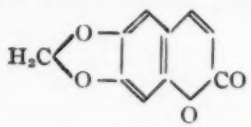
Herniarin (IX)

Considerable advantage has been gained by the discovery of "dicoumarol" (VIII), the haemorrhagic principle of "spoiled sweet clover" (improperly cured hay) which delays coagulation of blood[22]. Structurally dicoumarol is different from other natural coumarins in the sense that it has two coumarin nuclei bridged by a methylene group. It is the causative factor of what is known as the "sweet clover disease" in cattle. Dicoumarol is employed in medicine in the treatment of thrombosis and allied conditions and to control the bad effects of vitamin K_1. This anticoagulant probably acts by hindering the formation of prothrombin[23]. All coumarins having anti-vitamin K activity are metabolised in the body to salicylic acid which has a short-

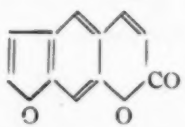
term action similar to that of dicoumarol[24]. The liver is the site of dicoumarol activity and this fact has been established by using a specimen having labelled carbon in the methylene group. But since it damages the liver, and its action is slow, search for synthetic compounds was stimulated. So far, the synthetic coumarin derivatives, known in trade as Tromexan, Cumopyran and Marcoumar, have been found to be much better remedies, which are active in small doses and free from the disadvantages of dicoumarol[25].

Dicoumarol is an effective rodenticide[26]. It is also a strong blastocholine for wheat and cress test plants. It inhibits growth and cell division in chicken fibroblast cultures[27]. In glaucoma, dicoumarol exerts an anticoagulant action on sclerotic and obliterative processes, thereby improving circulation in the eye and producing an enlargement of the visual field[28].

While dicoumarol is an anticoagulant, it is interesting to note that some simpler coumarins have the opposite effect. Herniarin (IX) and ayapin (X) have been found to possess a remarkable haemostatic property and are active both *in vitro* and *in vivo*. They are well tolerated by, and are non-toxic to, rabbits. Scopoletin, æsculetin dimethyl ether and daphnetin dimethyl ether also possess this property though the intensity of action is much less. The corresponding phenolic compounds are inactive. The mechanism of blood coagulation caused by these products is not known[29].



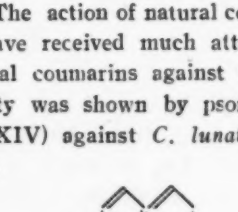
Ayapin (X)



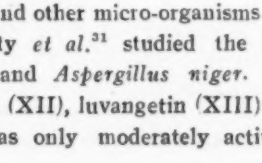
Psoralene (XI)

It is now generally recognized that the unsaturated lactonic structure is of frequent occurrence in pharmacologically important natural substances and is also encountered in some plant materials with bacteriostatic activity. Coumarin was found to have a low bacteriostatic activity, while dicoumarol inhibited the growth of *Bacillus anthracis*[30] in a dilution of 1 : 500,000.

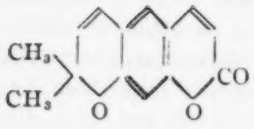
The action of natural coumarins on fungi and other micro-organisms does not seem to have received much attention. Chakraborty *et al.*[31] studied the action of 15 natural coumarins against *Curvularia lunata* and *Aspergillus niger*. The highest activity was shown by psoralene (XI), seselin (XII), luvangetin (XIII) and xanthyletin (XIV) against *C. lunata* while seselin was only moderately active against *A. niger*.



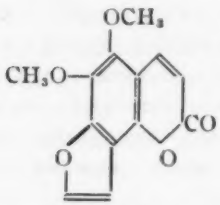
Seselin. (XII)



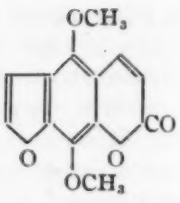
Luvangetin (XIII)



Xanthyletin (XIV)



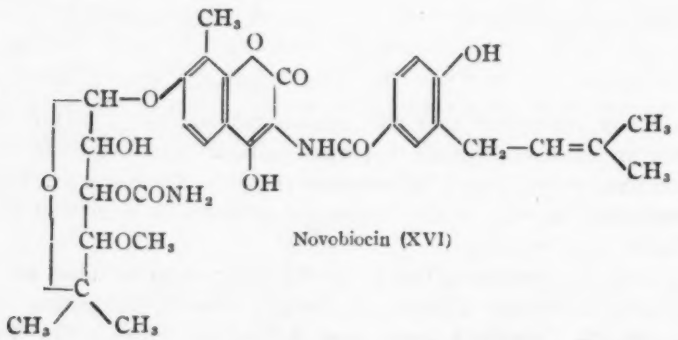
Pimpinellin (XV)



*iso*Pimpinellin (XV)

Dicoumarol has a decidedly antibacterial action. At a dilution of 1 : 50,000 it stopped the growth of *Staphylococcus aureus, S. albus* and *Streptococcus pyogenes*. It also inhibited the growth of *Pasteurella avicida* in a dilution of 1 : 25,000, but *Streptococcus faecalis* and some other organisms were not affected[32].

Novobiocin[33], a new antibiotic isolated from a *Streptomyces* sp., has been proved to be a coumarin derivative having the structure (XVI)[34]. The bacterial strains inhibited by this antibiotic include *Micrococcus, Streptococcus, Diplococcus, Neisseria, Corynebacterium, Pasteurella, Erysipelothrix* and *Proteus*[35]. Staphylococci are the most sensitive among the Gram-positive cocci. The antibacterial spectrum of this antibiotic corresponds generally with those of penicillin and erythromycin. But *in vitro* it is less potent than penicillin or erythromycin. It is equally effective by oral and subcutaneous route and is highly effective against Staphylococci resistant to other antibiotics.



Novobiocin (XVI)

The growth of *Staphylococcus aureus* was also inhibited by mesuol in a dilution of $3 : 10^6$. This substance is a coumarin derivative obtained from *Mesua ferrea* but its complete structure has not yet been determined. The substance is feebly active when compared with penicillin but almost as active as allicin, the antibiotic principle of garlic. It had no effect on the fungi, *A. niger, C. lunata, Alternaria solani* and *Helminthosporium sativum* [36].

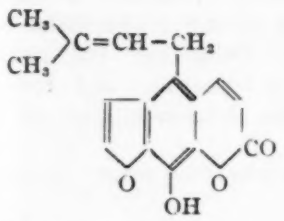
Calophyllolide, a complex coumarin isolated from *Calophyllum inophyllum*, showed tuberculostatic activity against a strain of *Mycobacterium tuberculosis* in a dilution of 1 : 20,000. The activity was lowered in presence of serum[37]. Tuberculostatic activity[38] is also exhibited by pimpinellin (XV) and *iso*pimpinellin (XVI) in

dilutions of $1:1\text{-}2\times10^{4}$. Æsculin can be used for the identification of bacteria, for it can be hydrolysed by some bacteria (*e.g.*, lactic acid bacteria, most streptococci and enterococci) producing æsculetin[39].

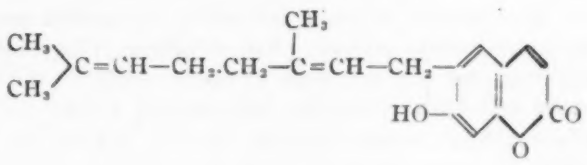
Coumarin and some of its derivatives having m.p.'s lower than 70-100° have been generally found to have strong anthelmintic action[40], while many natural coumarins, particularly those with a furan ring-system, are toxic to fish. Employing *Lebistes reticulatus* as test animals, Späth and Kuffner[41] observed the lethal effect of the following coumarins at the concentrations noted against them in 8 hours (Table II). In the early stage, the compounds exert a stimulant action, but soon the fish floats on its back, gradually stops moving and ultimately dies. Angelicin (XXIV), however, induces narcosis.

TABLE II

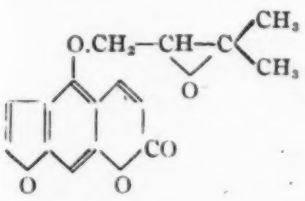
Coumarin	1 :6,800	Oxypeucedanin (XIX)	1 :70,000
Allo-imperatorin (XVII)	1 :40 000	Xanthotoxin (XX)	1 :70.000
Pimpinellin (XV)	1 :50,000	Imperatorin (XXI)	1 :74,000
*iso*Pimpinellin (XV*a*)	1 :60,000	Osthol (XXII)	1 :82,000
Ostruthin (XVIII)	1 :67,000	Bergapten (XXIII)	1 :93,000



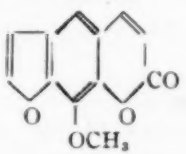
Allo-imperatorin (XVII)



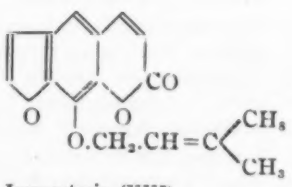
Ostruthin (XVIII)



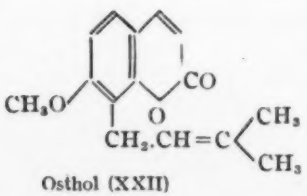
Oxypeucedanin (XIX)



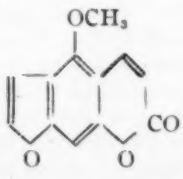
Xanthotoxin (XX)



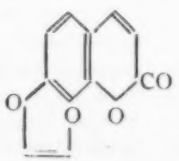
Imperatorin (XXI)



Osthol (XXII)



Bergapten (XXIII)



Angelicin (XXIV)

These results have been supplemented by Murti and Seshadri, who observed toxicity of umbelliferone and herniarin when tested against the fresh-water fish *Haplochitus panchax*[42].

Recently coumarins have figured prominently in the treatment of leucoderma. Oral and local administrations of psoralene-angelicin mixture obtained from *Psoralea corylifolia* have been reported to give beneficial results. *Ammi majus*, an Egyptian drug of value in the indigenous treatment of depigmented skin, has been found to contain the photo-sensitizing agents xanthotoxin, imperatorin and bergapten. The first two are said to hasten the formation of melanin. Comparatively, the active principles of *A. majus* are better than those of *Psoralea*. Though the complete cure rate is small, substantial improvement to the extent of 66% has been noticed in clinical trials[43].

The mechanism of action of these coumarins in stimulating pigmentation is not known. A full appraisal of the mechanism will no doubt encourage search for an effective curative drug. The Indian fruit, bael (*Aegle marmelos*), also contains imperatorin and allied compounds with a furan ring-system, and it may be worth while to study the behaviour of these compounds towards leucoderma.

This account of some interesting biochemical properties of natural coumarins is by no means complete. But, I believe, I have said enough to emphasize the fact that they are not mere metabolic products of the living cell but possess varied and often remarkable physiological actions. It is hoped that this review, although brief, would stimulate further studies of the biochemical aspects of coumarins, both natural and synthetic †.

† The assistance rendered by Shri D. P. Chakraborty in the preparation of this review is gratefully acknowledged.

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A STUDY OF THE CARBYLAMINE REACTION

By Sameer Bose

Carbylamine, produced in ethyl alcohol solution from various amino compounds under identical conditions, has been estimated by hydrolysing it to formic acid. The amount formed does not exceed 35% of the theoretical value and decreases considerably on dilution of the reaction mixture. Substitution of +I groups in aniline increases the yield whereas −I groups diminish it. In the mixture of iodoform and aniline, the reaction is induced photochemically in the absence of alkali. Urea has also been found to afford an *iso*nitrile.

There being no reference in literature to kinetics or even a quantitative treatment of often-used carbylamine reaction, it was felt that such a study might be fruitful. On allowing to react an alcoholic solution of potassium hydroxide with that of chloroform at 40° and determining the rate of disappearance of alkali acidimetrically, it was found that the rate remained practically unaltered by adding aniline to the reaction mixture. It appeared that the first step in the carbylamine reaction was the hydrolysis of chloroform and an intermediary, formed thereby, attacked the amine. As the nature and concentration of the intermediary was not known, a kinetic study was found impracticable. Hence, a quantitative study was undertaken in which carbylamine, produced under varying conditions of temperature and concentration of the reactants, was estimated. In all the experiments excess of chloroform was used and the reaction was carried out to complete consumption of the alkali.

Experimental

Evaluation of Carbylamine.—This was done by hydrolysing it in presence of dilute sulphuric acid and estimating the formic acid produced.

$$RNC + 2H_2O \rightarrow RNH_2 + H.COOH$$

Carbylamine was prepared mostly by treating in a 150 c.c. pyrex conical flask 3·5*N*-KOH (1 c.c.) with 0.4*M* amine solution (2 c.c.) and 40% $CHCl_3$ solution (1 c.c.) in EtOH at 56° for 3 hours during which time all the KOH was consumed. The flask was well stoppered during heating with a good compressed wood cork which was placed in position with a little pressure. For estimating carbylamine, the contents of the flask were cooled to 0° by placing it in crushed ice and then 25 c.c. of 0.1*N*-H_2SO_4 was pipetted into it with a fast pipette, the cork being lifted as little as possible. The acidified solution was again stoppered and heated at 56° for 8 hrs. In a few cases the cork yielded to the gas pressure inside, which necessitated repetition of the experiment. Later the contents were cooled to room temperature and titrated with 0.04*N*-NaOH solution, using phenolphthalein as indicator. A blank was carried out in an identical manner except for the addition of the amine solution, instead of which 2 c.c. of EtOH was used. In case of aniline, the values obtained for carbylamine were verified by estimating the residual aniline. After the formation of carbylamine, the contents of the flask were diluted with 25 c.c. of EtOH and boiled for about 10 minutes to drive off

all the carbylamine, as judged by its foul odour. An aliquot of the solution was then acidified with strong HCl solution and evaporated on a water-bath to a small bulk. The aniline hydrochloride remaining as residue was estimated by the bromine method (Stone, "Determination of Organic Compounds", 1956, p. 180). In Table I the values for carbylamine experimentally found are compared with those calculated from the aniline used up.

TABLE I

Estimation of carbylamine by acid hydrolysis.

(2 c.c. of 0.4*M* aniline soln. + 1 c.c. of KOH + 1 c.c. of 40% $CHCl_3$)

Normality of KOH soln.	3.5 *N*	3.0 *N*	2.7 *N*	2.5 *N*
Carbylamine found (c.c. of 0.04*M* soln.).	7.1	6.0	5.2	4.7
,, calc.	7.0	6.0	5.3	4.6

In cases of strong bases like methyl, ethyl and benzyl amines, the evaluation of carbylamine was done indirectly by titrating the remaining base with 0.1*N*-H_2SO_4 in presence of phenol red. A blank was carried out by heating the same volume of the solution of the base under identical conditions.

Effect of Dilution.—The formation of carbylamine from aniline was studied by treating 2 c.c. of 0.4*M* aniline solution with 1 c.c. of 2.9*N*-KOH and 1 c.c. of 40% $CHCl_3$ solution. The reaction mixture was diluted with varying quantities of alcohol, and heated at 56° till all the KOH was used up. The carbylamine produced diminished with dilution, as shown in Table II.

TABLE II

Alcohol added (c c.) for dilution ...	Nil	4	8	16
Carbylamine produced (c.c. of 0.04*M* soln.) ...	5.7	3.5	2.4	1.2

Effect of Concentrations of Aniline and KOH.—The reaction was first carried out by keeping the aniline concentration constant and changing that of the alkali. Later the aniline concentration alone was altered. Heating was carried out at 56° till the KOH was completely consumed. The results recorded in Table III reveal that the carbylamine produced increases with the increase in concentration of aniline and KOH, both.

TABLE III

(2 c.c. of aniline + 1 c.c. of KOH + 1 c.c. of 40% $CHCl_3$)

Aniline (*M*)	0.4	0.4	0.4	0.4	0.3	0.2	0.1
KOH (*N*)	0.8	1.8	2.6	3.5	3.5	3.5	3.5
Carbylamine produced (c.c. of 0.04*M* soln.)	1.3	2.8	4.8	7.0	4.0	2.5	1.8

Effect of Temperature.—The same concentrations of the amine, alkali and $CHCl_3$ were used for the reactions at 25°, 40° and 56°, and the time allowed for the reaction was 240, 50 and 3 hours respectively, when all the alkali was used up. The carbylamine produced was found to decrease slightly with increase in temperature, as shown in Table IV.

TABLE IV

(2 c.c. of 0.4*M* amine soln. + 1 c.c. of 3.5*N*-KOH + 1 c.c. of 40% $CHCl_3$)

Temp.	Carbylamine produced (c c of 0.04*M* soln.) Aniline.	*p*-Toluidine.	*m*-Toluidine.	*o*-Toluidine.
25°	7.9	8.2	7.4	6.8
40°	7.4	7.6	7.2	6.4
56°	7.1	7.4	7.0	5.2

Effect of Substitution.—Various substituted anilines and other amines were taken and carbylamine, produced under identical conditions, was estimated. The method adopted is comparable with the "Competition method", described by Ingold ("Structure and Mechanism in Organic Chemistry", 1953, p. 245) in connection with the action of HNO_2 on benzene and toluene. All the reactions were carried out at 56° and the time allowed was 3 hrs. In Table V the carbylamine produced has been given along with the strength of the base, expressed in terms of the Lowry-Brönsted system, as reported by Badger ("Structure and Reactions of Aromatic Compounds", 1954, p. 76, 196). The term $pK_a = -\log K_a$, where K_a is the acid dissociation constant of the base.

TABLE V

Heated at 56° for 3 hours. Other conditions same as in Table IV.

Base.	pK_a.	Carbylamine produced (c.c. of 0.04*M* soln.).	Base.	pK_a.	Carbylamine produced (c.c. of 0.04*M* soln.).
Aniline	4.6	7.1	*o*-Anisidine	4 5	7.4
o-Chloroaniline	2.8	4.7	*m*- ,,	4.2	7.4
m- ,,	2.1	5.6	*p*- ,,	5.3	8 4
p- ,,	3.5	5.8			
o-Nitroaniline	−0.2	2.7	α-Naphthol	4.0	3.7
m- ,,	2.6	4.7	β-Naphthol	4.3	5.4
p- ,,	1.1	2.7	Benzyl amine	9.4	7 1
o-Toluidine	4.4	5.2			
m- ,,	4.7	7.0	Methyl ,,	10.7	7.6
p- ,,	5.1	7.4	Ethyl ,,	10 7	7.4

Induced Photochemical Reaction.—It was felt that by extracting the halogen atoms from a methyl trihalide, an intermediary was produced which reacted with an amine to form carbylamine. Instead of alkali, this extraction could be carried out photochemically as well, in presence of O_2. A benzene solution of CHI_3 in the presence of sunlight and O_2 was found to decompose completely into free I_2 and an unknown product. When dilute solutions were taken (0.1 − 0.05%) the iodine obtained was quantitative, but in case of stronger solutions iodine liberated gave a deep red or violet colour to the solution which acted as an "autofilter" and prevented further

action of light. This difficulty was overcome by adding aqueous solution of hypo to the benzene solution and shaking the mixture occasionally. This photochemical oxidation was found to take place in all organic solvents, but in case of benzene and ether it was comparatively rapid. The unknown product, formed after extracting all the I_2 photochemically from CHI_3, was found to produce carbylamine in the presence of an amine. A strong solution of CHI_3 (10 c.c.) in benzene, taken in a 150 c.c. pyrex conical flask, was treated with 0.2*N* hypo solution (10 c.c.) and 4 drops of aniline. The mixture was exposed to sunlight with occasional shaking. The O_2 enclosed in the flask was sufficient for the photo-oxidation and in about 15 minutes a distinct smell of carbylamine was obtained. The reaction took place in the absence of hypo solution as well, but the smell of carbylamine obtained was very faint. Toluidines, when similarly treated, also gave carbylamine.

DISCUSSION

Vorländer and Guthke (*Ber.*, 1929, **62B**, 549) reported that an alcoholic solution containing $CHCl_3$ and KOH possessed a strong reducing power which could not be accounted for by the mere presence of H.COOH, formed during the reaction. They postulated the formation of HO.CHO (hydroxyformaldehyde), an aldehydic isomer of H.COOH, as an intermediate product and also claimed to have precipitated it with methone. Hine (*J. Amer. Chem. Soc.*, 1950, **72**, 2438) has presented a strong case in favour of the view that CCl_2 is produced as an intermediary. The formation of a highly reactive compound like activated CO, HO.CHO or CCl_2 is undeniable. This intermediate compound attacks the amine :

$$(1)\quad HO.CHO + RNH_2 \longrightarrow RNC + 2H_2O$$
$$(2)\quad HO.CHO \longrightarrow H.COOH.$$

As shown above, there are two competing reactions taking place. These seem to possess different temperature coefficients and molecularity, because the yield of carbyl amine varies with temperature and dilution.

The quantity of carbylamine produced was found to depend upon the basic strength of the amine (Table V). The basic property of the NH_2 gr up is associated with the lone pair of electrons available on the nitrogen for forming the bond with the proton (Pauling, "The Nature of the Chemical Bond", 1952, p. 206). The formation of carbylamine also seems to depend on the availability of this lone pair of electrons. Negative substituents (Cl and NO_2) in aniline produce a mesome. c effect which attracts this lone pair of electrons towards the $-I$ group and consequently diminishes the yield of carbylamine. The NO_2 group leads to a preferential diminution of electron density at *ortho* and *para* positions (Badger, *loc. cit.*, p. 199). Therefore *ortho*- and *para*-nitroanilines should furnish a poorer yield of carbylamine than the *meta*-isomer. This fact has been borne out experimentally (Table V). Very similar considerations apply to the positive substituents which generally release electrons and increase the yield.

A *meta*-methoxy group is base-weakening whereas *para*-methoxy is base-strengthening (Badger, *loc. cit.*, p. 204) ; hence, the yield of carbylamine should be more in *p*-anisidine, as already found. The effect of methyl substituent also is more marked in the

para position because in this position the mesomeric and inductive effects reinforce one another and increase the electron density. The highest yield of carbylamine among the toluidines was from the *para* compound.

The carbylamine reaction is not afforded by the amides, because the lone pair of electrons belonging to the nitrogen atom shifts towards the carbon and from there to the oxygen atom (Pauling, *loc. cit.*, p. 133). This electron displacement causes weakening of the basic strength of the NH_2 group. It would therefore appear that wherever there is a lone pair of electrons available on the nitrogen atom (in NH_2 group), carbylamine reaction must take place. Urea possesses slightly basic properties, because the electrons of one of the two NH_2 groups shift towards the carbon atom, but the same is not true of the other group. Hence, urea should also form carbylamine. This fact was experimentally verified and positive results were obtained. When urea (10 g.) was heated with 3.4*N* alcoholic KOH (5 c.c.) and 25% $CHCl_3$ solution (5 c.c.), a highly toxic gas with a foul odour, like aliphatic carbylamines, was evolved.

The photochemically induced reaction can be explained on the assumption that CHI_3 on photo-oxidation in sunlight produces free I_2 and an active isomer of CO which reacts with an amine to give carbylamine. Emschwiller (*Bull. soc. chim.*, 1939, *v*, **6**, 561) reported that equal volumes of CO and CO_2 were produced along with free I_2 during the photo-oxidation. An attempt to isolate the unknown carbon compound produced, by extracting it with ether, failed as the same appeared to be gaseous.

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A STUDY IN THE COMPLEX FORMATION OF BERYLLIUM IONS WITH HYDROXY-CARBOXYLIC ACIDS

By I. D. Varma and R. C. Mehrotra

It has been shown by electrometric titrations that compared to aliphatic α-hydroxy-acids, salicylic acid is a better chelating agent for beryllium ions. The nature of complexes formed by beryllium with salicylate ions has been investigated in detail by electrometric and conductometric titrations, and a plausible mechanism has been suggested for the titration curves obtained. The correctness of the suggested mechanism has been demonstrated by quantitative analysis of the products of various reactions. Alternative and more convenient methods have been described for the preparation of the complex salts : $Be[Be(C_7H_4O_3)_2].4H_2O$ or $Be(C_7H_4O_3).2H_2O$ and $K_2[Be(C_7H_4O_3)_2]\cdot H_2O$.

Although studies have recently been carried out on the complexes formed by beryllium ions in aqueous solutions (Takeshi and Furuhata, *Bull. Inst. Phys. Chem. Res., Japan*, 1943, **22**, 367; Purkayastha, this *Journal*, 1947, **24**, 257; Meek and Banks, *J. Amer. Chem. Soc.*, 1951, **73**, 4108), not much systematic physicochemical work, however, appears to have been carried out on the complexes formed by beryllium ions with salicylic acid and other aliphatic α-hydroxy-acids like glycollic acid and its substituted products, lactic and mandelic acids. A survey of the literature reveals that the preparations of some complex salts of the above acids with beryllium have already been described (Parson and Sargent, *J. Amer. Chem. Soc.*, 1909, **31**, 1203; Rosenheim and Lehmann, *Annalen*, 1924, **440**, 153; Jones *et al.*, *J. Phys. Chem.*, 1930, **34**, 563; Asmussen and Madsen, *Z. anorg. Chem.*, 1933, **212**, 321).

The nature of complex species present, when beryllium ions are treated with salicylate ions in aqueous solution, has been investigated by the following electrometric and conductometric titrations :

(*i*) Electrometric titration of beryllium sulphate ($BeSO_4$) and basic beryllium sulphate $Be(OH)(SO_4)_{0.5}$ with salts of salicylic acid and other aliphatic α-hydroxy acids.

(*ii*) Electrometric and conductometric titration of beryllium sulphate alone and in the presence of 1, 2 and 4 moles of potassium salicylate with alkali.

Experimental

Beryllium sulphate (B.D.H.-Analar) was crystallised three times from conductivity water and analysed. The analyses corresponded to $BeSO_4.4H_2O$. Salicylic acid (B.D.H.-Analar) was also crystallised from hot conductivity water. The solution of potassium salicylate was prepared by dissolving the requisite amount of salicylic acid in an equivalent quantity of KOH solution. Standard solutions of Be(OH)Cl and $Be(OH)(SO_4)_{0.5}$ were obtained by adding one equivalent of the alkali to a standard solution of normal beryllium salts and making up to a known volume.

p_H measurements were carried out in a thermostatically controlled room (temp. 25° ± 1°) with a Philips p_H-measuring apparatus, G.M. 4491/G.M. 4493. A glass electrode gave readings reproducible to ± 0.005 p_H.

Conductometric measurements were carried out in a thermostat (35° ± 0.1°) with the help a of resistance measuring assembly, Philips G.M. 4429 and an Emerson cell, G.M. 4221.

Electrometric Titration.—Electrometric titrations were carried out by adding the reagent from a micropipette to 20 c.c. of the solution containing beryllium ions. The p_H was noted after stirring gently the solution for two minutes and waiting for another two minutes. Two such readings were obtained for every addition of the reagent, and these were found to be almost identical in every case. For sake of brevity the actual p_H observations and the plotted graph (Table I ; curve 1, Fig. 1) are both recorded here for one system only and for the rest, only the graph has been given.

TABLE I

System : 20 c.c. of $M/40$-$BeSO_4$ + K-salicylate.

$M/2$-$C_7H_5O_3K$ added.	p_H of the system.	$M/2$-$C_7H_5O_3K$ added.	p_H of the system.
0.0 c.c.	3.435	1.5 c.c	3.015
0.1	3.125	1.6	3.030
0.2	3.015	1.7	3.045
0.3	2.975	1.8	3.060
0.4	2.955	1.9	3.075
0.5	2.945	2.0	3.090
0.6	2.945	2.2	3.125
0.7	2.945	2.4	3.160
0.8	2.950	2.6	3.190
0.9	2.955	2.8	3.220
1.0	2.965	3.0	3.255
1.1	2.975	3.2	3.295
1.2	2.985	3.4	3.325
1.3	2.995	3.6	3.355
1.4	3.005	3.8	3.385
		4.0	3.415

Conductometric Titrations.—The conductometric titrations were carried out by adding $M/2$ alkali from a micropipette to a solution of beryllium sulphate ($M/80$, 40 c.c.) in presence of the requisite quantity of potassium salicylate. The solution was stirred for fifteen minutes and left for another five minutes before noting the readings. Such an operation gave constant values for every reading as well as ensured that the solution attained the temperature of the bath fully. Here also, the actual readings (Table II ; curve 2, Fig. 3) are given for one system only, and for the rest, only graphs are shown in Fig. 3.

TABLE II

System : 40 c.c. of $M/80$-$BeSO_4$ + 1 c.c. K- sal. + NH_4OH.

$M/2$-NH_4OH added.	$1/R$ of the system $\times 10^{-3}$.	$M/2$.NH_4OH added	$1/R$ of the system $\times 10^{-3}$.
0.0 c.c.	3.533	2.2 c.c.	5.813
0.2	3.636	2.4	5.813
0.4	3.676	2.6	5.813
0.6	3.802	2.8	5.813
0.8	3.845	3.0	5.813
1.0	4.000	3.2	5.813
1.2	4.347	3.4	5.813
1.4	4.739	3.6	5.813
1.6	4.926	3.8	5.813
1.8	5.236	4.0	5.813
2.0	5.586		

$Be[Be(C_7H_4O_3)_2.4H_2O$ *or* $Be(C_7H_4O_3)_2.2H_2O$.—To a solution of $BeSO_4$ (2.2141 g. in 500 c.c. H_2O) containing 25 c.c. of $M/2$-$C_7H_5O_3K$ (molar ratio of $BeSO_4$: $C_7H_5O_3K$ = 1 : 1) was added gradually 12.5 c.c. of M-KOH solution (1 mole). The reaction mixture was concentrated to 50 c.c. From the concentrate, potassium sulphate was completely precipitated by addition of 100 c.c. of absolute alcohol. The filtrate was allowed to evaporate to dryness at 60° to a white shining crust. The crust was powdered and repeatedly crystallised from conductivity water to give crystals of $Be[Be(C_7H_4O_3)_2]$ or $Be(C_7H_4O_3)_2$, dried at 90-95° and cooled in a desiccator. The compound is hygroscopic, sparingly soluble in water, alcohol, benzene and acetone. {Found : Be, 5.195. Calc. for $Be[Be(C_7C_4O_3)_2].4H_2O$: Be, 4.98%}. This confirms the fact that the reaction among $BeSO_4$ (1 mole), $C_7H_5O_3K$ (1 mole) and KOH (1 mole) may be represented as :

$$BeSO_4 + C_7H_5O_3K + KOH \rightarrow \tfrac{1}{2}\, Be\,[Be(C_7H_4O_3)_2] + K_2SO_4 + H_2O.$$

$K_2[Be(C_7H_4O_3)_2]$.—(*a*). To a solution of $BeSO_4$ (2.215 g. in 500 c.c.) containing 25 c.c. of $M/2$-$C_7H_5O_3K$ (molar ratio of $BeSO_4$: $C_7H_5O_3K$ = 1 : 1) was added gradually 25 c.c. of M-KOH (2 moles). The solution was left for 2 hours after which the precipitated mass was filtered off, washed with cold water and ignited to BeO. The filtrate was concentrated to 50 c.c. On addition of 100 c.c. of absolute alcohol to the concentrate, potassium sulphate was completely precipitated. On evaporation of the alcoholic filtrate to dryness at 60°, a faintly pink crust was obtained. It was finally powdered and repeatedly crystallised from water and dried at 100°, and cooled in a desiccator. A white crystalline powder, soluble in water, dilute mineral acids, moderately soluble in alcohol and sparingly soluble in ammonia and alkalies, was obtained which was analysed. {Found : Be, 2.38 ; K, 20.81 ; $C_7H_4O_3$, 74.01. Calc. for $K_2[Be(C_7H_4O_3)_2].H_2O$: Be, 2.38 ; K 20.71 ; $C_7H_4O_3$, 72.12%}.

Alkaline permanganate was used for determination of salicylate ions (Bottger and Oesper, "Newer Methods of Volumetric Chemical Analysis", pp. 55-65).

The reaction among $BeSO_4$ (1 mole), $C_7H_5O_3K$ (1 mole) and KOH (2 moles), represented by the following equation, was further confirmed by estimating the amount of precipitated beryllium hydroxide, the amounts of complex salt $K_2[Be(C_7H_4O_3)_2]$ and also of K_2SO_4 formed in the reaction.

$$BeSO_4 + C_7H_5O_3K + 2\ KOH \rightleftharpoons \tfrac{1}{2}\ Be(OH)_2 + K_2SO_4 + H_2O + \tfrac{1}{2}\ K_2\ [Be(C_7H_4O_3)_2]$$

(*b*). To a solution of $BeSO_4$ (2.217 g. in 500 c.c. H_2O) containing 50 c.c. of *M*/2-$C_7H_5O_3K$ (molar ratio of $BeSO_4$: $C_7H_5O_3K$ = 1 : 2) was added gradually 25 c.c. of *M*-KOH (2 moles). The clear solution, thus obtained, was concentrated to 50 c.c. Potassium sulphate was completely precipitated by addition of absolute alcohol to the concentrate. The filtrate (free of K_2SO_4) was allowed to evaporate at 60°, yielding a white crust which was dried at 100° and cooled in a desiccator. The product was purified by crystallisation from water. The crystalline powder, which was similar to the complex salt described above, was obtained and analysed. { Found : Be, 2.38 ; K, 20.80 ; $C_7H_4O_3$, 74.0. Calc. for $K_2[Be(C_7H_4O_3)_2]\ H_2O$: Be, 2.38 ; K, 20.71 ; $C_7H_4O_3$, 72.12% }.

The fact that the following reaction among $BeSO_4$ (1 mole), $C_7H_5O_3K$ (2 moles) and KOH (2 moles) is quantitative, has been further shown by estimating the amount of K_2SO_4 and the complex salt formed by known amounts of the reactants :

$$BeSO_4 + 2\ C_7H_5O_3K + 2\ KOH \rightarrow K_2[Be(C_7H_4O_3)_2] + K_2SO_4 + 2H_2O$$

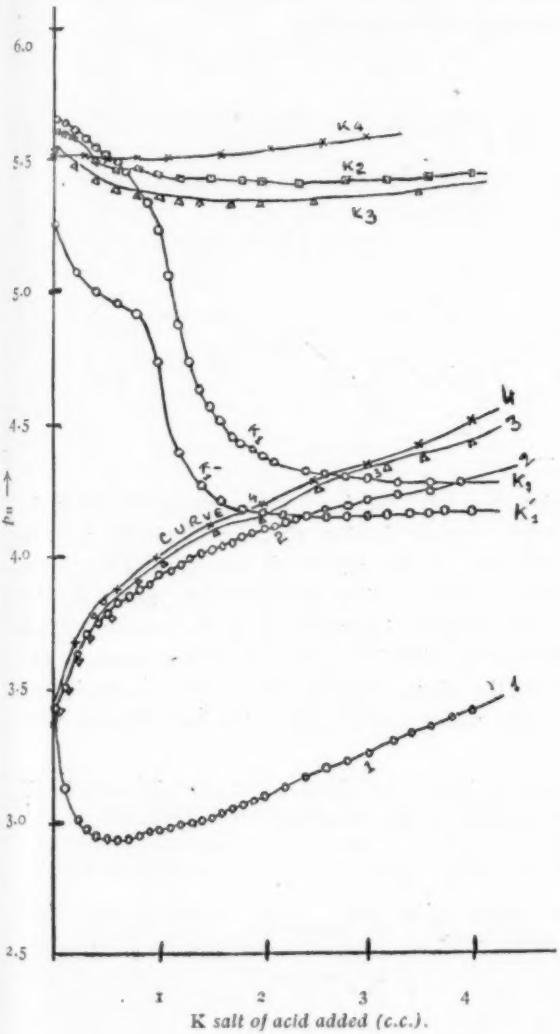
Discussion

The electrometric titration of beryllium sulphate with potassium salicylate (curve 1, Fig. 1) indicates a chelation of the type

... (1)

This chelation by the donation of a lone pair of electrons from the hydroxyl oxygen atom makes the "hydrogen" atom more labile and acidic, and thus, the extent of lowering in the p_H of the system (curve 1, Fig. 1) is a direct measure of the above type of chelation. As shown in a recent study with zirconium mandelate (Kapoor and Mehrotra, *J. Sci. Ind. Res.*, 1957, **16B**, 304), also the extent of chelation increases with the rise of p_H of the solution (curves 1 and K_1, Fig. 1). A comparison of curves K_1, K_2, K_3 and K_4 and also of 1, 2, 3 and 4 (Fig. 1) indicate that chelation of the above type is much less in the case of aliphatic hydroxy-acids (glycollic, lactic and mandelic acids) compared to salicylic acid.

FIG. 1



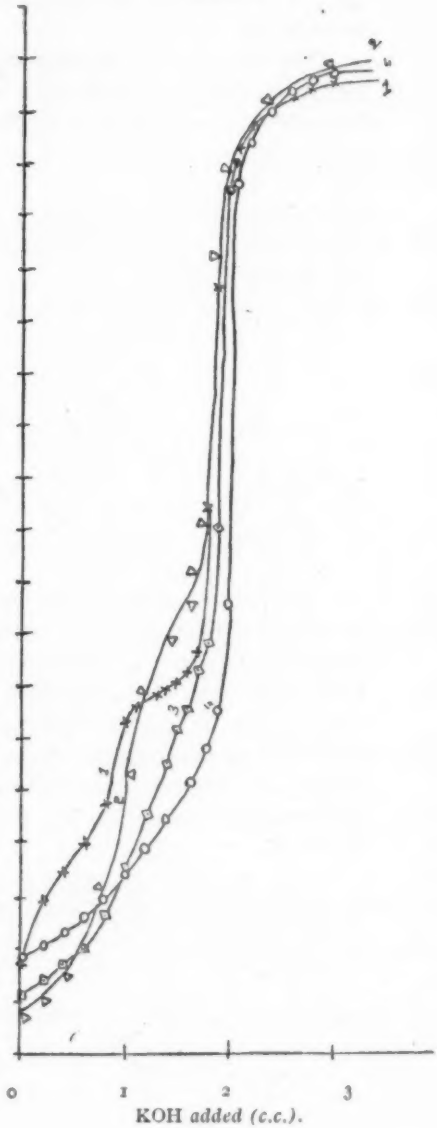
K *salt of acid added (c.c.).*

Curves 1, 2, 3 and 4: 20 c.c. $M/40$-$BeSO_4.4H_2O$ soln. titrated with $M/2$-K salts of salicylic, mandelic, glycollic and lactic acids, respectively.

Curves K_1, K_2, K_3 and K_4: 20 c.c. $M/40$-$Be(OH)(SO_4)_{0.5}$ soln. titrated with $M/2$-K salts of the respective acids as above.

Curve K_1: 20 c.c. $M/40$-Be(OH)Cl titrated with $M/2$-K-Sal. soln.

FIG, 2

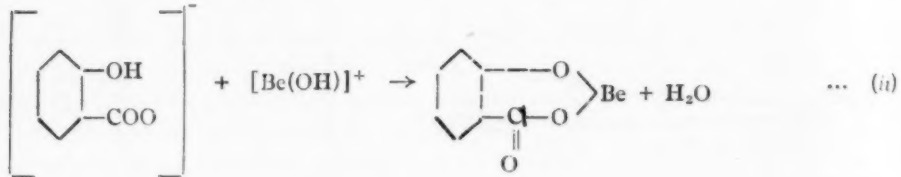


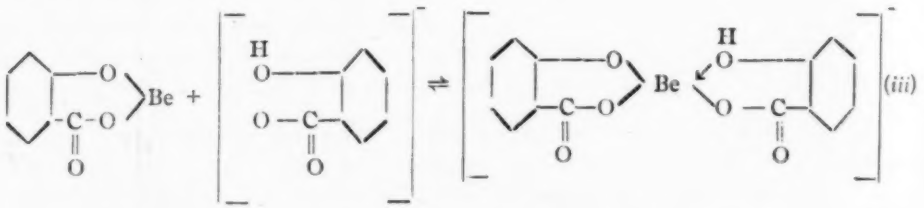
KOH *added (c.c.).*

Curves 1-4: Titration of 20 c.c. $M/40$-$BeSO_4.4H_2O$ soln. containing 0, 1, 2 and 4 moles of $C_7H_5O_3K$ respectively with $M/2$-KOH soln.

In view of the strong chelation shown by salicylate ions, it was considered of interest to investigate the system more fully. The results obtained can be explained as noted below.

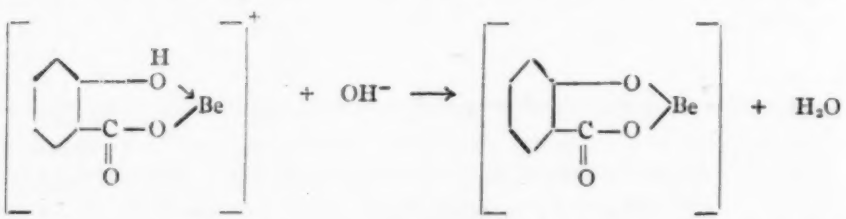
The electrometric titration (curve K_1, Fig. 1) of $Be(OH)(SO_4)_{0.5}$ with potassium salicylate ($C_7H_5O_3K$) indicates a small fall in p_H for the first mole of salicylate and a comparatively large fall in p_H for the second mole of salicylate.



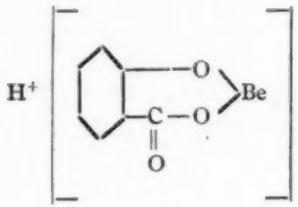


The fall in p_H in the above titration, however, continues even after the second mole of salicylate has been added. This might indicate further chelation of another mole of salicylate, but this is very improbable due to the maximum covalency of beryllium being four. The above therefore indicates that further amount of salicylate shifts the equillibrium (*iii*) to the right, and thus slightly lowers the p_H of the medium. This conclusion is supported by the results of the titrations also. That the anion of the beryllium salts does not take part in the above complex formation is shown by the similar nature of the curve K'_1 (Fig. 1) in which case Be(OH)Cl has been titrated with $C_7H_5O_3K$.

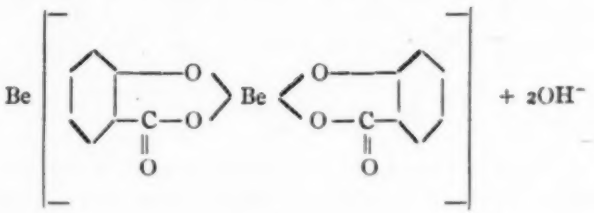
The electrometric titration (curve 2, Fig. 2) of [$BeSO_4$ + $C_7H_5O_3K$] with KOH indicates a slow rise in p_H of the solution initially due to the following neutralisation :

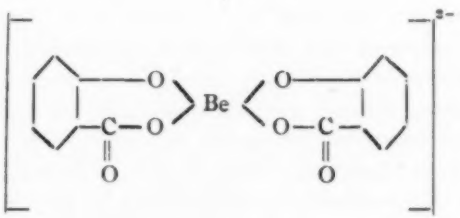


The above mechanism is supported by the isolation of beryllium salicylate ($BeC_7H_4O_3$) by the treatment of one mole of $BeSO_4$ with a mole each of $C_7H_5O_3K$ and KOH. The p_H (3.4) at half neutralisation indicates the dissociation constant of the order of $10^{-3.4}$ (3.5×10^{-4}) for the corresponding acid :



The neutral beryllium monosalicylate may be assigned the alternative structure $Be[Be(C_7H_4O_3)_2]$ (Jones *et al., loc. cit.*). This easily explains the titration curve 2 (Fig. 2). After the addition of the first mole of alkali, the titration curve is quite similar to the titration curve of beryllium sulphate itself with alkali (curve 1, Fig. 2), and it may therefore be explained by the following simple reaction :

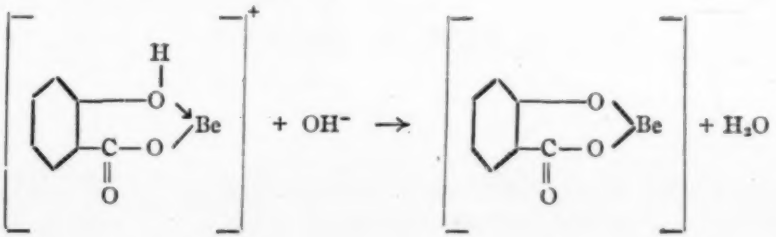


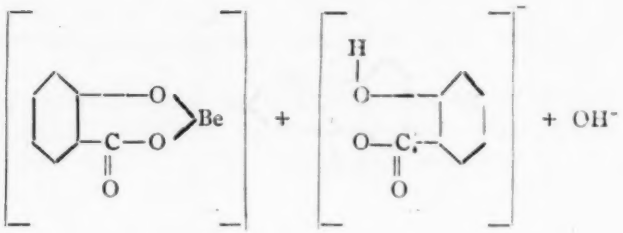


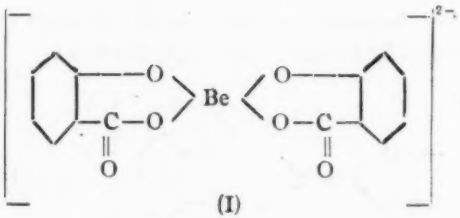
+ $Be(OH)_2$ ... (*iv*)

The above conclusions have been further supported by the isolation of $Be(OH)_2$ and $K_2[Be(C_7H_4O_3)_2]$ almost in equimolecular quantities when $BeSO_4$ is treated with two moles of KOH in presence of 1 mole of $C_7H_5O_3K$.

The titration (curve 3, Fig. 2) of $BeSO_4$ with alkali in presence of 2 moles of $C_7H_5O_3K$ can be explained simply as :





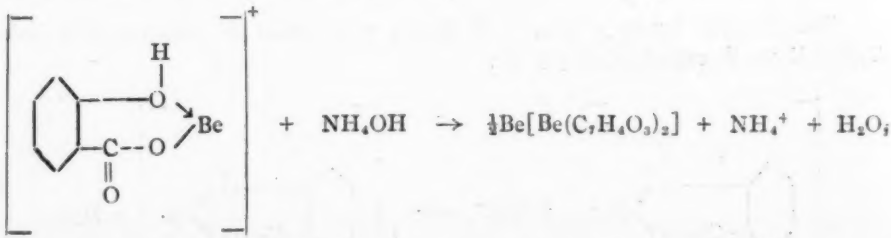


(I)

The stability of (I) is indicated by the non-precipitation of $Be(OH)_2$ even after the p_H of the medium exceeds 11 in the presence of higher hydroxyl-ion concentration. The titration (curve 4, Fig. 2) in the presence of 4 moles of salicylate ions confirms the above conclusion. The earlier portion of the curve 4 is higher than curve 3 due to the presence of basic salicylate ions, but in the range of 1-2 moles, this effect is counterbalanced and even surpassed due to the shift of equilibrium (v) to the right.

The conductometric titrations on similar systems were first carried out with potassium hydroxide, but these did not provide sharp inflection points (curves K_1, K_2 and K_3, Fig. 3). When potassium hydroxide was replaced by the weak base, ammonium hydroxide, the above titration yielded very sharp inflection points. As the excess of ammonium hydroxide increases the conductivity of the medium only very negligibly, the end-point is indicated very sharply.

The titration (curve A_1, Fig. 3) of $BeSO_4$ with NH_4OH in presence of 1 mole of $C_7H_5O_3K$ can be explained on the following lines:



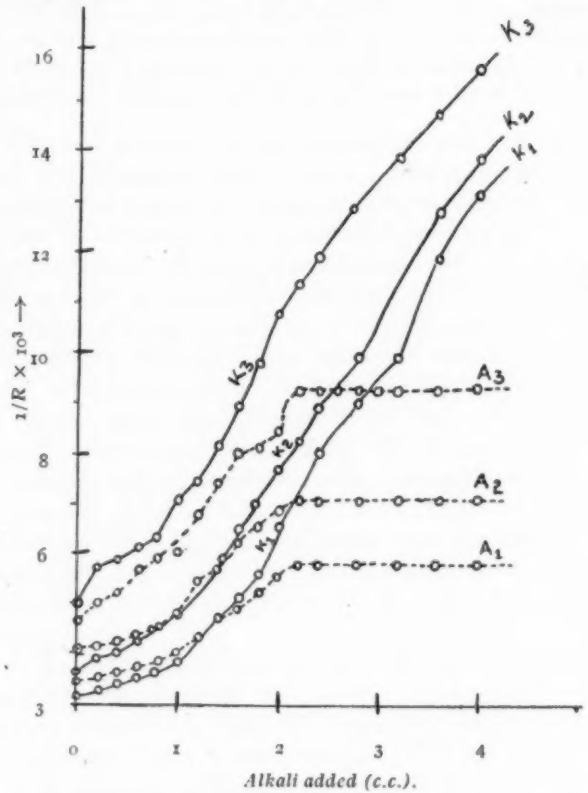
showing a small rise in conductivity due to replacement of complex beryllium ion bya smaller NH_4^+. The neutral beryllium monosalicylate has a very small conductivity

as shown by Jones *et al. (loc. cit.)*. With a further mole of NH_4OH the following reaction may be assumed to be occurring :

$$\tfrac{1}{2}\,Be[Be(C_7H_4O_3)_2] + NH_4OH \longrightarrow \tfrac{1}{2}\,[Be(C_7H_4O_3)_2]^{2-} + NH_4^{+} + \tfrac{1}{2}\,Be(OH)_2$$

(showing a large rise in conductivity)

FIG. 3



Curves K_1, K_2 and K_3: Titration of 40 c.c. of $M/80$-$BeSO_4.4H_2O$ soln. containing 1, 2 and 4 moles respectively of $C_7H_5O_3K$ with $M/2$-KOH soln.

Curves A_1, A_2 and A_3: Titration of 40 c.c. of $M/80$-$BeSO_4.4H_2O$ soln. containing 1, 2 and 4 moles respectively of $C_7H_5O_3K$ with $M/2$-NH_4OH.

The titration (curve A_2, Fig. 3) in the presence of 2 moles of $C_7H_5O_3K$ is similar to A_1 although showing a less sharp inflection at 1 mole, indicating that beryllium salicylate anion begins to get formed at an earlier stage. This inflection point disappears in curve

A_3 in the presence of excess of salicylate ions, indicating the formation of disalicylate ion from almost the beginning. The titration curve is almost horizontal after the addition of 2 moles of NH_4OH in every case, indicating that no higher complexes are formed in the system. The above conclusions from conductometric work therefore are in full accord with the conclusions from electiometric and preparative experiments.

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SYNTHESIS OF 5-METHOXY-2-INDANONE

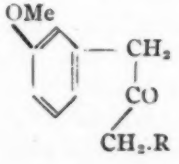
By Amareshwar Chatterjee, Ramesh Chandra Chatterjee* and Bidyut Kamal Bhattacharyya

1-Bromo-3-(*m*-methoxyphenyl)-propan-2-one on treatment with anhydrous aluminium chloride affords *m*-methoxybenzylmethyl ketone. Ethyl *m*-methoxyphenylacetate, on chloromethylation, followed by oxidation, furnishes 4-methoxyphthalic and methoxyterephthalic acids. The cyano-esters, obtained from the above chloro-esters, are converted into a mixture of the crystalline diacetic acids (IV : $R=R_1=CH_2.CO_2H$; $R_2=H$ and $R=R_2=CH_2.CO_2H$; $R_1=H$). *m*-Methoxybenzyl chloride on chloromethylation, followed by treatment with potassium cyanide and then hydrolysis, furnishes the same mixture of diacetic acids. The dimethyl esters of the latter, on cyclisation, afford an isomeric mixture of β-keto esters which are hydrolysed to the same indanone (II : $R=R_1=H$).

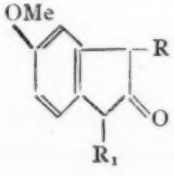
With the object of synthesising the degradation and the dehydrogenation product of Jervine (cf. Chatterjee, Chatterjee and Bhattacharyya, this *Journal*, 1957, **34**, 855) the preparation of 5-methoxy-2-indanone is reported below.

The cyclisation of 1-bromo-3-(*m*-methoxyphenyl)-propan-2-one (I : R=Br), prepared from *m*-methoxyphenylacetyl chloride, diazomethane and hydrobromic acid, to the indanone (II : $R=R_1=H$) by anhydrous aluminium chloride resulted in the formation of *m*-methoxybenzylmethyl ketone (I : R=H), identified by comparing its semicarbazone (m.p. 137-38°) with that of an authentic sample, prepared from *m*-methoxyphenylacetyl chloride and diethyl malonate (Wilds and Close, *J. Amer. Chem. Soc.*, 1947, **69**, 3079). Behal and Tiffeneau (*Bull. soc. chim.*, 1908, *iv*, **3**, 314) reported to have obtained the same ketone (I : R=H) by the action of mercuric oxide and iodine on *m*-methoxyphenylpropylene. The semicarbazone of their ketone has been described to melt at 175°. The failure to cyclise the bromoketone (I : R=Br) to the indanone (II : $R=R_1=H$) is in agreement with the observation of Smith and Wilson (*J. Chem. Soc.*, 1955, 1342) who report that for the conversion of α-bromo-α'-phenylalkyl ketone into 2-indanone, the activation of bromine by a suitable α-substituent appears necessary.

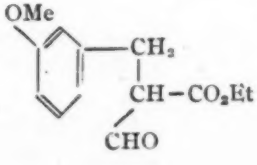
Being unable to cyclise the above bromo-ketone in the expected way, experiments were modelled after Robinson and Crowley (*ibid.*, 1938, 2001 ; cf. Koo and Hartwell, *J. Amer. Chem. Soc.*, 1953, **75**, 1625), but, unfortunately, the cyclisation of ethyl α-formyl-β-(*m*-methoxyphenyl)-propionate (III) under acidic conditions always resulted in a polymeric product. The desired indanone was finally prepared as described below.



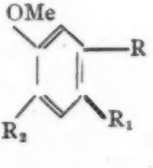
(I)



(II)



(III)



(IV)

* In part.

The chloromethylation of ethyl *m*-methoxyphenylacetate yielded a mixture of chloro compounds (IV : R=$CH_2.CO_2Et$; R_1=CH_2Cl ; R_2=H and R=$CH_2.CO_2Et$; R_1=H ; R_2=CH_2Cl) in low yield. To establish the orientation of the chloromethyl group, the above mixture of the chloro compounds was oxidised to 4-methoxyphthalic and methoxyterephthalic acids. The mixture of the chloro-esters was converted into the corresponding cyano-esters which after esterification, followed by hydrolysis, furnished crystalline diacetic acids (IV : R=R_1=$CH_2.CO_2H$; R_2=H and R=R_2=$CH_2.CO_2H$; R_1=H) ; but the chloromethylation of *m*-methoxybenzyl chloride, under controlled condition, afforded in moderately good yield a mixture of dichloro compounds (IV : R=R_1=CH_2Cl ; R_2=H and R=R_2=CH_2Cl ; R_1=H) which was oxidised to the above phthalic acids. The above dichloro compounds were converted by the method of Moore and Thorpe (*J. Chem. Soc.*, 1908, **93**, 165) into a mixture of dinitriles, hydrolysis of which by acid or base furnished a poor yield of the aforementioned mixture of the diacetic acids ; but the conversion of the nitriles to the esters, followed by hydrolysis, afforded a better yield. The desired indanone (II : R=R_1=H) was obtained in poor yield by heating the lead salts of the above mixture of the diacetic acids.

The separation of the diacetic acids to pure components was very difficult, but the sodioenolates of the β-keto esters (II : R=H ; R_1=CO_2Me and R=CO_2Me ; R_1=H), produced by the Dieckmann cyclisation of the esters (IV : R=R_1=$CH_2.CO_2Me$; R_2=H and R=R_2=$CH_2.CO_2Me$; R_1=H), may be easily separated from the unchanged ester (IV : R=R_2=$CH_2.CO_2Me$; R_1=H). With this end in view the mixture of dimethyl esters, obtained from the above diacetic acids, was subjected to the Dieckmann reaction to furnish sodioenolates, insoluble in benzene. The aqueous solution of the enolates on acidification furnished, probably, a mixture of isomeric β-keto esters (II : R=CO_2Me ; R_1=H and R=H ; R_1=CO_2Me) which were separated by fractional crystallisation. Both the β-keto esters separately on hydrolysis afforded the same desired indanone (II : R=R_1=H). The oxidation of one of the isomeric β-keto esters yielded 4-methoxyphthalic acid.

The attempted alkylation of one of the β-keto esters gave a mixture of products which could not be characterised. The Mannich-Robinson reaction with the indanone or with the β-keto esters was not promising, always yielding a polymerised product (Harradence and Lions, *J. Proc. Roy. Soc., N. S. Wales*, 1939, **72**, 284; Wenkert and Bhattacharyya, *J. Amer. Chem. Soc.*, 1956, **78**, 797).

EXPERIMENTAL*

1-Bromo-3-(m-methoxyphenyl)-propan-2-one (I : R=Br).—A mixture of *m*-methoxyphenylacetic acid (10 g.) in dry benzene (12 c.c.), pyridine (3 drops) and thionyl chloride (7.6 c.c.) was allowed to stand at room temperature for 3 hours, warmed at 40-50° for half an hour and distilled to furnish the acid chloride, b.p. 120°/2 mm, yield 6.8 g. To the dry ethereal solution of diazomethane, prepared from nitrosomethylurea (20 g.), cooled in a freezing mixture, was added the above acid chloride

* All m.p.'s are uncorrected. The ultraviolet absorption spectrum was examined in 95% ethanol by the Unicam spectrophotometer, S.P. 500.

(4 g.), the mixture allowed to stand for 1 hour and then treated with hydrobromic acid (48%) till the evolution of nitrogen had ceased. After 16 hours at room temperature, the reaction mixture was washed with dilute sodium carbonate solution and water, and dried over sodium sulphate. The residue, obtained after evaporation of the solvent, was evaporatively distilled at 130-40°/2.5 mm to furnish the bromo-ketone (2 4 g.). The analytical sample was evaporatively distilled at 130-35°/2 mm. (Found: Br, 32.31. $C_{10}H_{11}O_2Br$ requires Br, 32.92%). The bromo-ketone did not furnish a semicarbazone by the pyridine method.

Attempted Cyclisation of the Bromo-ketone (I: R=Br).—To a stirred anhydrous aluminium chloride (1.98 g) in tetrachloroethane (10 c.c.), cooled in an ice-bath, was added dropwise during half an hour a solution of the bromo-ketone (1.2 g.) in tetrachloroethane (3 c.c.). The reaction mixture was allowed to stand for 16 hours and then it was decomposed by cold dilute hydrochloric acid and extracted with ether. The organic layer was washed with dilute alkali, then water and dried. After removal of the solvent, the residue was evaporatively distilled at 75-85°/1.5 mm to furnish an oil (0.88 g.) which responded to the test for halogen. The oil was treated with semicarbazide hydrochloride in pyridine and methanol to furnish a semicarbazone (0.75 g.), m.p. 124-25° which was refluxed for 6 hours with an aqueous solution of oxalic acid (35 c.c., 20%). The resulting oil was extracted with ether. The ethereal layer was washed with sodium carbonate solution and water, and dried. The oily residue, after removal of the solvent, was evaporatively distilled at 70-80°/1.5 mm to afford *m*-methoxybenzylmethyl ketone in 0.4 g. yield. (Found: C, 73.16; H, 7.44. $C_{10}H_{12}O_2$ requires C, 73.17; H, 7.31%).

The *semicarbazone*, prepared from the above ketone (0.1 g.), was crystallised three times from dilute methanol, m.p. 137-38°. (Found: C, 59.82; H, 6.83; N, 19.02. $C_{11}H_{15}O_2N_3$ requires C, 59.72; H, 6.78; N, 19.0%).

m-*Methoxybenzylmethyl Ketone* (I: R=H).—To sodio-malonic ester, prepared from sodium (1.4 g.) and diethyl malonate (14 g.) in ether (60 c.c.), was added with stirring *m*-methoxyphenylacetyl chloride (1.02 g) at room temperature. The reaction mixture, after being kept standing for 16 hours, was acidified with cold dilute acetic acid. The ethereal layer was separated and the aqueous layer was extracted three times with a mixture of benzene and ether. The combined extract was washed with water and the oily residue, on removal of the solvent, was refluxed with a mixture of glacial acetic acid (30 c.c.), HCl (conc., 30 c.c.) and water (12 c.c) for 2 hours. The cold reaction mixture was diluted with water and the precipitated oil was thoroughly extracted with ether-benzene mixture. The organic layer was washed with base and water, and dried. On removal of the solvent, the residue was evaporatively distilled at 70-80°/1.5 mm to yield a colorless ketone (0.8 g.). The *semicarbazone* of this ketone, m.p. 137-38°, prepared in the usual manner, did not depress the m p. of the sample obtained above.

Ethyl α-Formyl-β-(m-methoxyphenyl)-propionate (III).—Ethyl β-(*m*-methoxyphenyl)-propionate was prepared in better yield in the following way:

A mixture of *m*-methoxybenzaldehyde (27.2 g.), cyanoacetic ester (22.4 g.), ammonium acetate (8 g.), glacial acetic acid (9.6 c.c.) and benzene (400 c.c.) was refluxed for 4 hours. The reaction mixture was worked up to furnish a yellow oil (40 g.), b.p. 185-89°/2 mm which was then hydrogenated over palladium on charcoal catalyst (10%) in ethanol solution. The crude saturated cyano-ester (40 g.) was hydrolysed by refluxing with HCl (conc., 400 c.c.) for 40 hours and the crude acid, thus obtained, was methylated with dimethyl sulphate and alkali to furnish the pure crystalline acid (26 g.), b.p. 160°/1 mm, m.p. 45-46°; Johnson *et al.* (*J. Amer. Chem. Soc.*, 1952, **74**, 2251) recorded m.p. 44-46°. The ethyl ester (22 g.), b.p. 135-40°/2.5 mm, was obtained by refluxing the acid (22 g.) with absolute ethanol (100 c.c.) and H_2SO_4 (conc., 6 c.c.).

To sodium ethoxide, prepared from sodium dust (3.45 g.), absolute alcohol (8.6 c.c.) and benzene (60 c.c.), cooled in an ice-bath, was added with constant shaking a solution of the above ethyl ester (14.6 g.) and ethyl formate (12.9 c.c.) in dry ether (60 c.c.). The reaction mixture, after being kept standing for 48 hours at room temperature, was diluted with cold water. The aqueous layer was separated and extracted once with ether. The organic layers were combined and washed with 5% NaOH solution (cold and dilute). The unchanged propionic ester (5 g.) was obtained from the organic layer. The combined aqueous and alkaline solutions were acidified with HCl (cold and dilute) and saturated with ammonium chloride. The precipitated oil was extracted three times with ether and the ethereal layer was washed with water and dried. The residual oil, obtained after evaporation of the solvent, gave the formyl compound (8 g.), b.p. 135-40°/0.6 mm, which exhibited a strong violet coloration with alcoholic ferric chloride solution. (Found: C, 65.69; H, 7.05. $C_{13}H_{16}O_4$ requires C, 66.10; H, 6.77%).

Attempts were made to cyclise the above formyl compound in the following manners:

(*i*). To a mixture of phosphoric acid (*d* 1.75, 5 c.c.) and H_2SO_4 (conc., 1.3 c.c.), cooled in a freezing mixture, was added the formyl compound (1.4 g.). After 2 hours the reaction mixture was worked up to afford a polymerised product.

(*ii*). The attempted cyclisation of the formyl compound by heating at 240-50°/40 mm resulted in the isolation of the unchanged material.

(*iii*). The formyl compound was mixed with polyphosphoric acid (10 g.) at 0° and after 1 hour the reaction mixture was worked up to give a polymerised product.

(*iv*). The cold solution of the formyl compound (1 g.) in absolute methanol (20 c.c.) was saturated with dry HCl gas. The reaction mixture was allowed to stand for 16 hours in the refrigerator, refluxed for 6 hours and then worked up with ether to furnish an oil (0.18 g.), evaporatively distilling at 105-15°/1 mm; λ_{max} 307 mμ (log ϵ 3.96); but no crystalline acid could be obtained on treatment with base.

Ethyl 3-Methoxy-6-chloromethyl- and 3-Methoxy-4-chloromethyl-phenylacetates (IV: $R=CH_2CO_2Et$; $R_1=CH_2Cl$; $R_2=H$ and $R=CH_2.CO_2Et$; $R_1=H$; $R_2=CH_2Cl$)

(*a*). Dry HCl gas was passed through a mixture of ethyl *m*-methoxyphenylacetate (5 g.), formalin (40%, 3 c.c.), zinc chloride (0.3 g.) and ether (25 c.c.) at room tempera-

ture for half an hour for complete saturation. When the reaction mixture warmed up, it was cooled in an ice-bath. The ethereal layer was washed with water, sodium carbonate solution (10%) and water. After removal of the solvent, the residue was fractionated: (*i*) unchanged material (0.5 g.), b.p. 105-110°/0.6 mm; (*ii*) desired compound (1.7 g.), b.p. 130-40°/0.6 mm. (Found: Cl, 14.12. $C_{12}H_{15}O_3Cl$ requires Cl, 14.63%). Using the same quantities of the materials but saturating it in the cold, the yield of the desired chloro compound was 1.22 g.

(*b*). Dry hydrogen chloride was passed through a mixture of ethyl *m*-methoxyphenylacetate (5 g.), paraformaldehyde (0.5 g.) and ether (30 c.c.) at room temperature till saturation. The reaction mixture was worked up to furnish the chloro compound (0.64 g).

Oxidation of the Chloro-esters.—To the chloro-ester (1 g.) was added slowly a solution of $KMnO_4$ (4.8 g.) and NaOH (8 g.) in water (120 c.c.). The reaction mixture was heated on the steam-bath for 6 hours, made colorless with ethanol and filtered. The precipitated manganese dioxide was washed thoroughly with hot water. The filtrate was concentrated, acidified and extracted repeatedly with ether. After evaporation of the solvent, the gummy residue was treated with ether when a fraction went into solution leaving a white solid, m.p. 280-85°, which was crystallised three times from hot water to furnish colorless prisms of methoxyterephthalic acid (0.06 g.), m.p. 293-95°. (Found: C, 55.53; H, 4.31. Calc. for $C_9H_8O_5$: C, 55.10; H, 4.08%). The ether-soluble fraction was crystallised three times from a mixture of ether and petroleum ether (b.p. 60-80°) to afford 4-methoxyphthalic acid (0.2 g.), m.p. 169-70°. (Found: C, 55.41; H, 4.27. Calc. for $C_9H_8O_5$: C, 55.10; H, 4.08%).

3-Methoxy-6-chloromethyl- and 3-Methoxy-4-chloromethyl-benzyl Chlorides (IV: $R=R_1=CH_2Cl$; $R_2=H$ and $R=R_2=CH_2Cl$; $R_1=H$).—Dry HCl gas was passed rapidly (if the rate of flow of the gas is slow then the whole of the material will polymerise) through a mixture of *m*-methoxybenzyl chloride (28 g.), zinc chloride (2 g.), formalin (17 c.c.) and ether (100 c.c.) at room temperature for 1 hour to completely saturate it. After sometime the reaction mixture warmed up. It was worked up as before and fractionated: (*i*) unchanged material (5.2 g.), b.p. 80-82°/0.8 mm; (*ii*) the dichloro compounds (29 g.), 115-20°/0.8 mm. (Found: Cl, 34.15. $C_9H_{10}OCl_2$ requires Cl, 34.63%).

Utilising *m*-methoxybenzyl chloride (4.5 g.), formalin (2.4 c.c.), zinc chloride (0.3 g.) and ether (35 c.c.) and cooling the reaction mixture, when warmed up, the desired product (3.05 g.) was obtained. No reaction took place when paraformaldehyde was substituted for formalin, and the reaction was carried out, as described above, in an ice-bath.

Oxidation of the above mixture of the dichloro compounds (1 g.), as described before, furnished 4-methoxyphthalic acid (0.35 g.), m.p. 169-70° and methoxyterephthalic acid (0.1 g.), m.p. 293-95°.

3-Methoxybenzene-1:6- and -1:4-diacetonitriles (IV: $R=R_1=CH_2.CN$; $R_2=H$ and $R=R_2=CH_2.CN$; $R_1=H$).—To a boiling solution of potassium cyanide (30 g.) in

a mixture of water (40 c.c.) and ethanol (120 c.c.) were added dropwise the above dichloro compounds (30 g.) in such a way that the heat of reaction kept the reaction mixture boiling. After the addition was complete, the mixture was allowed to reflux for half an hour more. The cooled reaction mixture was diluted with water and the precipitated oil was extracted with ether. The ethereal layer was washed with water and dried. The solvent was evaporated and the residue was distilled, b.p. 160-70°/0.2 mm. On redistillation it furnished pure dinitriles (16 g.), b.p. 160-62°/2 mm. (Found: N, 14.68. $C_{11}H_{10}ON_2$ requires N, 15.05%).

3-Methoxybenzene-1:6- and -1:4-diacetic Acids (IV: $R=R_1=CH_2.CO_2H$; $R_2=H$ and $R=R_2=CH_2.CO_2H$; $R_1=H$).—(*a*). The mixture of diethyl esters (9.3 g., b.p. 155-65°/0.4 mm), prepared by refluxing the above dinitriles (12 g.), double distilled ethanol (100 c.c.) and H_2SO_4 (conc., 20 c.c.) for 16 hours, was not completely free of nitrogen. It was refluxed with a solution of KOH (18 g.) in a mixture of water (20 c.c.) and methanol (150 c.c.). The reaction mixture was worked up to give solid dicarboxylic acids (6 g.), m.p. 148-50°, a part of which was crystallised four times from ether-benzene mixture, m.p. 158-59°. (Found: C, 59.01; H, 5.63. $C_{11}H_{12}O_5$ requires C, 58.92; H, 5.35%).

(*b*). A mixture of the chloro-esters (IV: $R=CH_2CO_2Et$; $R_1=CH_2Cl$; $R_2=H$ and $R=CH_2.CO_2Et$; $R_1=H$; $R_2=CH_2Cl$; 2.25 g.), acetone (50 c.c.), potassium cyanide (1.5 g.), sodium iodide (0.2 g.) and water (2.4 c.c.) was refluxed for 20 hours. The solvent was removed under reduced pressure. The residue, after dilution with water and acidification with HCl (cold, dil.), was extracted with a mixture of ether and benzene. The organic layer was washed with water and distilled. The dry residue was refluxed with a mixture of double distilled ethanol (15 c.c.) and H_2SO_4 (conc., 3 c.c.) to furnish an oil (0.85 g.) which was hydrolysed with methanol (9 c.c.), KOH (1 g.) and water (1 c.c.), as described above, to give a solid acid, m.p. 140-45°, which on crystallisation yielded a pure mixture of acids, m.p. 158-59°, the mixed m.p. of which with those described above remained undepressed.

Dimethyl 3-Methoxybenzene-1:6- and -1:4-diacetates (IV: $R=R_1=CH_2CO_2Me$; $R_2=H$ and $R=R_2=CH_2CO_2Me$; $R_1=H$).—The mixture of the above crude acids (3.8 g.) was esterified with diazomethane, prepared from nitrosomethylurea (8 g.), in ethereal solution to yield the esters (4 g.), b.p. 150-52°/0.6 mm. (Found: C, 61.48; H, 6.68. $C_{13}H_{16}O_5$ requires C, 61.90; H, 6.34%).

Methyl 5-Methoxy-hydrind-2-one-1- and -3-carboxylates (II: $R=H$; $R_1=CO_2Me$ and $R=CO_2Me$; $R_1=H$).—To sodium methoxide, prepared from sodium dust (1.08 g.) under dry benzene and absolute methanol (1.46 c.c.), were added dropwise with shaking under nitrogen the dimethyl esters (4 g.) in dry benzene (15 c.c.). The reaction which started at the room temperature was completed by refluxing on a water-bath for 2 hours. The reaction mixture was cooled and the precipitated enolate was dissolved in cold water. The benzene layer was separated and the aqueous layer was extracted twice with ether. On removal of organic solvent, the residue was distilled (1 g.), b.p.

150°/0.6 mm. The aqueous solution on acidification with cold dilute acetic acid furnished a material (m.p. 95-100°), which on evaporative distillation at 130-35°/1.5 mm yielded a crystalline material, m.p. 95-105°. The latter gave a deep blue colour with alcoholic ferric chloride solution and on fractional crystallisation from methanol gave (*i*) a β-keto ester (0.5 g.), m.p. 97-98° (Found: C, 65.20; H, 5.62. $C_{12}H_{12}O_4$ requires C, 65.45; H, 5.45%); (*ii*) another less soluble β-keto ester (350 mg.), m.p. 126-27° (Found: C, 65.21; H, 5.63. $C_{12}H_{12}O_4$ requires C, 65.45; H, 5.45%).

5-Methoxy-2-indanone (II: R=R$_1$=H).—(*a*). The β-keto ester (0.2 g., m.p. 97-98°) was refluxed with 20% H_2SO_4 (5 c.c.) for 4 hours under nitrogen. The cooled reaction mixture was diluted with water and then extracted thrice with ether. The organic layer was washed with cold saturated sodium bicarbonate solution and water, and dried. The solvent was distilled and the residue was evaporatively distilled at 80-90°/1.5 mm to furnish a crystalline ketone (0.12 g.), m.p. 75-80°. The methoxy-indanone, thus obtained, developed in presence of air a brown colour within a very short time. It developed a deep blue colour, characteristic of β-indanone system (Moore and Thorpe, *loc. cit.*) with H_2SO_4 (conc.) containing a trace of an oxidising agent. The *semicarbazone* (0.1 g.), m.p. 218-19°, obtained from the above ketone (0.1 g.), was crystallised three times from methanol, m.p. 226-27°. (Found: N, 19.40. $C_{11}H_{13}O_2N_3$ requires N, 19.17%).

The other isomeric β-keto ester furnished the same ketone, m.p. 75-80°, on similar hydrolysis.

(*b*). The acids (IV: R=R$_1$=$CH_2.CO_2H$; R$_2$=H and R=R$_2$=$CH_2.CO_2H$; R$_1$=H; 0.4 g.) were well mixed with dry lead carbonate (0.4 g.) in a sublimation tube. The air was displaced with nitrogen and the tube was introduced in a heating bath maintained at 300-305°. After 10 minutes a colorless oil came over. It solidified after sometime, m.p. 75-80°. It was characterised through its semicarbazone.

The β-keto ester (200 mg., m.p. 97-98°) was oxidised as before to yield 4-methoxyphthalic acid (0.04 g.), m.p. 169-70°.

Attempted Methylation of the β-Keto Ester.—To the enolate, prepared from the β-keto ester (0.88 g.), m.p. 97-98°, sodium dust (0.1 g.), dry benzene (20 c.c.), under nitrogen, was added methyl iodide (2 c.c.). The reaction mixture was refluxed for 5 hours and diluted with water. The aqueous layer was extracted twice with ether and the combined extract was washed with aqueous NaOH solution (5%) and water, and dried. The solvent was evaporated and the residue (0.75 g.) was hydrolysed as before to yield an oil (0.3 g.), evaporatively distilling at 100°/0.2 mm. The oil was converted into the semicarbazone, m.p. 215-17°, which on five crystallisations from dilute methanol afforded a material in 0.017 g. yield, m.p. 238-39°. The analysis (Found: N, 14.47%) definitely indicated that it was neither pure nor homogeneous.

Attempted Mannich-Robinson Reaction.—(*a*). The reaction of methoiodide of 1-diethylamino-3-butanone (0.53 g. of base) in benzene (8 c.c.) with 5-methoxy-2-indanone (0.6 g.) in methanolic sodium methoxide (5 c.c., 0.136 g. of Na) under nitrogen furnished only a polymerised product.

(*b*). A methanolic solution of the enolate of the β-keto ester, m.p. 97-98° (0.41 g ; Na, 0.042 g.) was allowed to react with the methoiodide (0.28 g. of base) in methanol. The reaction mixture was allowed to stand for 20 hours, refluxed for one hour and then worked up to furnish an oil (0.6 g) ; λ_{max} 280 mμ. The latter on treatment with glacial acetic acid and HCl gave an oil (0.02 g.), evaporatively distilling at 160°/0.2 mm, which failed to furnish a semicarbazone.

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A STUDY OF THE HYDROGEN BONDING IN *o*-NITROPHENOL IN PRESENCE OF *p*-NITROPHENOL

By S. M. Deshpande and N. V. Parthasarathy

The individual polarograms of *o*- and *p*-nitrophenols in the p_H range of 1.0 to 10 2 have been studied. The polarograms of mixtures of the two phenols at p_H 10.2 and 2.0 have also been studied. These consist of single waves and are of similar pattern, and exhibit residual current region.

With increasing amounts of *o*-nitrophenol in an excess of *p*-nitrophenol or *vice versa*, the wave-heights increase gradually, although the value is less than the sum total of the individual wave-heights. Thus, a mutual influence of the two substances in mixtures is observed, the influence of the *ortho* compound over the *para*- isomer being less than the reverse.

The stability the of H-bonding in *o*-nitrophenol varies with the porportional amount of *p*-nitrophenol. The influence of *para* over the *ortho* compound results in the destabilisation of the H-bonding in the latter.

Ortho- and *para*-nitrophenols have been studied by several workers (Shikata *et al.*, *J. Agrl. Chem. Japan*, 1928, **4**, 924 ; *Mem. Coll. Agrl. Kyoto Imp. Univ.*, 1931, **17**, 121 ; Astle and McConnell, *J. Amer. Chem. Soc.*, 1943, **65**, 35, 2395; Pearson, *Trans. Faraday Soc.*, 1948, **44**, 692 ; 1949, **45**, 199 ; Page *et al.*, *J. Phys. Coll. Chem.*, 1949, **53**, 545). *o*-Nitrophenol possesses a H-bonded structure which is absent in the *p*-isomer, and this difference accounts for the variation in their melting point and solubility ("Handbook of Chemistry and Physics", 1952 ; Carric, *J. Phys. Chem.*, 1921, **25**, 628) and complex formation (Phillip, *J. Chem. Soc.*, 1903, **83**, 820; 1924, **125**, 527). As any other factor, the presence of *para*- isomer is likely to influence the formation and stability of the H-bonding in *o*-nitrophenol, and hence, a polarographic study of the above influence has been undertaken.

For a study of such influence, a knowledge of the polarographic behaviour of individual substances is necessary. The earlier workers differ in their results and views, e.g. Page *et al.* (*loc. cit.*) report that *ortho*-nitrophenol is reduced to the $-NH_2$ compound in acid media in one stage, while Pearson (*loc. cit.*) reports that this takes place in two stages. Astle and McConnell (*loc. cit.*) point out that *ortho*-nitrophenol is reduced to -NHOH stage alone in acid media, which is attributed to the stabilisation of this product by H-bond (Sidgwick, "Organic Chemistry of Nitrogen Compounds", 1942, p. 268). But Pearson points out that the above H-bonded structure is reducible further. In neutral solutions, while Page *et al.* report the reduction of *ortho*-nitrophenol in one stage to -NHOH only, others do not report about the nature of the reduction in this medium. As regards reduction of *p*-nitrophenol, while Page *et al.* report a 6*e* reduction in acid media in one stage (*i.e.* to $-NH_2$ stage), Pearson reports reduction in two stages as in nitrobenzene (Shikata, *Trans. Faraday*

Soc., 1925, **21**, 42, 53). These workers differ also in the values of their half-wave potentials and the slopes of the p_H—half-wave potential curves.

On account of such divergent results the present authors have studied the two nitrophenols first individually and then in mixtnres under identical sets of conditions with the equipment available.

EXPERIMENTAL

Individual Phenols

A manual type of polarograph, supplied by Adept Laboratories, Poona, was used for the investigation. It consists of the usual features, viz., potential divider, galvanometer, the dropping mercury electrode and the polarographic cell. The circuit diagram involved is the usual one. The capillary characteristic is 1.373 mg.$^{2/3}$/sec. $^{1/2}$, the drop time beiug 3.8 secs. An Ayrton shunt 1/20 was used in all the studies except where otherwise indicated. The galvanometer sensitivity was 4.3×10^{-8}amp./cm.

All experiments were carried out with $5 \times 10^{-3}M$ stock solutions of the nitrophenols in 10% ethanol. The test solution consisted of 4 c.c. of the stock solution mixed with 4 c.c. of 0.009 % gelatin solution and 12 c c. of buffer. The measurements were carried out with buffers of p_H 1.0, 2.0, 3.0, 4.2, 4.8, 5.6, 7.2, 8.0, 9.3 and 10.2, the p_H of the buffers being checked by Merck's indicators and charts. Gelatin was iucluded in the solution to suppress maxima.

The test solution was deaerated by bubbling hydrogen for 15 minutes, the dropping mercury electrode dipped into the solution and the polarographic cell connected to a saturated calomel electrode (S.C. E.), used as the reference electrode by an agar bridge. The temperature of the cell was maintained constant at 27° ± 1°. The polarogram of the solution was recorded. The diffusion current was measured by extrapolation method. The number of electrons involved in the electrode reaction was evaluated by means of the Ilkovic equation (*Coll. Czech. Chem. Comm.*, 1934, **6**, 498). The diffusion coefficients of the nitrophenols have been evaluated from the relation

$$D = \frac{2.990 \times 10^{-7}}{\eta (V_m)^{1/3}} \text{ at } 27°$$

where η is the viscosity of the solution and V_m, the molar volume of the nitrophenol. The diffusion coefficients of *o*- and *p*-nitrophenols, thus calculated, are 7.254×10^{-6} and 7.290×10^{-6} cm^2/sec. respectively.

Mixtures of o- *and* p-*Nitrophenols*

The test solution was prepared by mixing 4 c.c. of the stock solution ($5 \times 10^{-3}M$) of *o*-nitrophenol with 1 c.c. of 0.036% gelatin solution and 12 c.c. of buffer of p_H 10.2. To this mixture 0.5, 1.0, 1.5, 2.0 ..... 4 c.c. of *p* nitrophenol solutions (5×10^{-3} *M*) were added in successive experiments, and the total volume of the mixture was made up to 20 c.c. The test solution was then deaerated by bubbling hydrogen and the polarograms were recorded.

A set of polarograms with 4 c.c. of the stock solution of *p*-nitrophenol and varying amounts of *o*-nitrophenol solution at the same p_H have also been recorded.

The above two sets of experiments were then performed at p_H 2.0. A few of the polarograms are recorded in Fig. 3. The wave-heights are recorded in cm of the galvanometer scale and this multiplied by 0.86 gives the diffusion current (or wave-height) in microamperes.

Chemically pure substances were employed in all the above studies.

TABLE I

Polarographic study of o- *and* p-*nitrophenols individually in* 10% *ethanol at various* p_H.

p_H.	No. of waves.	Half-wave potential ($E_{\frac{1}{2}}$) (in volts)		Diffusion current (i_D) (in m. amp.)		No. of electrons (n).	
		1st. step.	2nd. step.	1st. step.	2nd. step.	1st. step.	2nd. step.
				A. *o*-Nitrophenol.			
1.0	1	−0.175	...	14.20×0.86	...	5.4	...
2.0	1	−0.205	...	11.70	...	4.5	...
3.0	1	−0.290	...	10.70	...	4.1	...
4.2	1	−0.310	...	10.20	...	3.9	...
4.8	1	−0.370	...	11.20	...	4.2	...
5.6	2	−0.410	−0.710	3.00	5.80×0.86	1.8	3.4
7.2	1	−0.520	...	9.10	...	3.5	...
8.0	1	−0.560	...	9.00	...	3.5	...
9.3	1	−0.640	...	9.50	...	3.6	...
10.2	1	−0.720	...	9.20	...	3.5	...
				B. *p*-Nitrophenol.			
1.0	1	−0.255	...	15.5×0.86	...	5.9	...
2.0	1	−0.330	...	13.0	...	5.0	...
3.0	1	−0.360	...	13.0	...	5.0	...
4.2	1	−0.450	...	12.0	...	4.6	...
4.8	1	−0.490	...	12.0	...	4.6	...
5.6	2	−0.510	−1.010	4.8	7.4×0.86	1.8	4.7
7.2	1	−0.670	...	15.8	...	3.9	...
8.0	1	−0.725	...	13.4	...	3.3	...
9.3	1	−0.820	...	11.7	...	4.5	...
10.2	1	−0.990	...	10.6	...	4.1	...

DISCUSSION

Individual Phenols

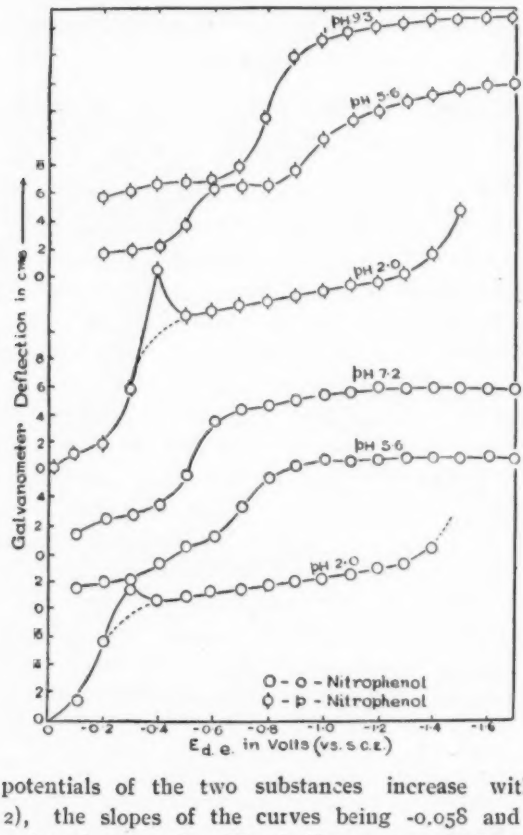
The half-wave potentials, number of electrons involved in the electrode reaction (n) and the wave-heights are recorded in Table I (A and B). A few of the polarograms are shown in Fig. 1.

The polarograms of both *o*- and *p*-nitrophenols consist of single waves in the p_H range 1.0 to 10.2 except at p_H 5.6, where a double-wave is indicated (vide Fig. 1).

Maxima were observed in good acid media in spite of the presence of gelatin as the maximum suppressor.

FIG. 1

Polarograms of o- & p-*nitrophenols in* 10% *ethanol at various* p_H.

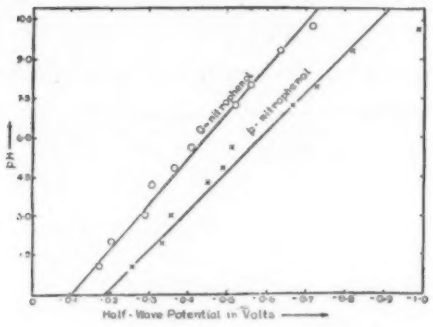


The half-wave potentials of the two substances increase with p_H and vary linearly (vide Fig. 2), the slopes of the curves being -0.058 and -0.067V/p_H unit respectively for *o*- and *p*-nitrophenols. The half-wave potentials and wave-heights of the *ortho*-compound are always less than those of the *para*-isomer (vide Table I, A and B), and this is attributed to the H-bonding (Sidgwick, *loc. cit.*) in *o*-nitrophenol.

Further, from the values of (n) in Table I, it is evident that *o*-nitrophenol is reduced in one stage to $-NH_2$ at low p_H (1.0 and 2.0) and to -NHOH stage only at p_H 3.0 to 5.0. *p*-Nitrophenol is reduced to $-NH_2$ directy in acid media. Reduction of both the substances proceeds through the intermediary nitroso state at p_H 5.6, the final stage being the -NHOH state in the two cases. Both the substances are reduced at one stage to —NHOH in neutral and alkaline media, *i.e.* from p_H 7.2 to 10.2.

FIG. 2

Effect of p_H on half-wave potential.



Mixture of Phenols

The half-wave potentials and wave-heights of the mixtures of *o*- and *p*-nitrophenols at p_H 10.2 and 2.0 are recorded in Table II. The %influence is computed to the sum total of the wave-heights of the two nitrophenols observed separately (vide Table I).

Polarograms at p_H 10.2.—The polarograms of mixtures observed at p_H 10.2 consist of single waves (vide Fig. 3) and are of similar pattern and contain residual current region.

The observed wave-heights are always less than the sum total of the proportional wave-heights of the substances in the mixtures. It is therefore inferred that the above decrease in the wave-heights is due to the influence of one over the other.

Considering the structures of the two substances, *o*-nitrophenol contains a H-bond, whereas the *para*-isomer is devoid of the same. The presence of *ortho*- may have very little influence over *para*-nitrophenol since the stability of the *para*-isomer is greater as compared to that of the *ortho*-isomer, as supported by the physical properties such as m.p. and steam-volatility. *p*-Nitrophenol, however, is likely to influence the stability of *o*-nitrophenol.

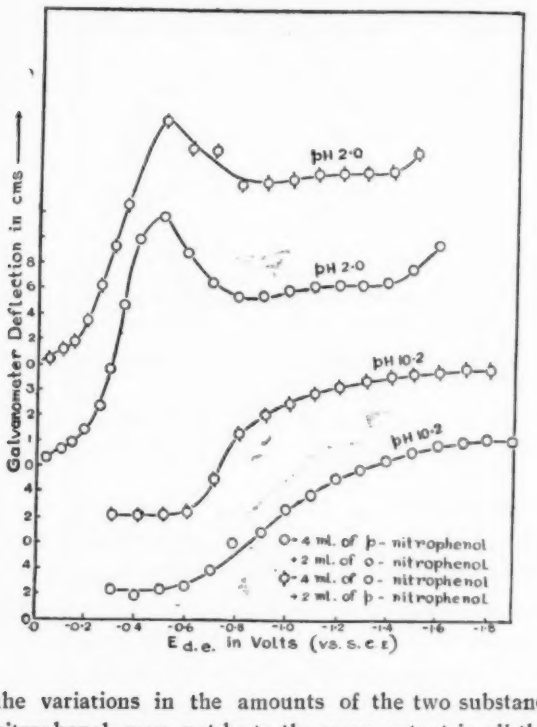
In the first set of experiments, wherein varying amounts of *ortho*-phenol are added to a constant amount of *p* isomer, the %influence calculated remains more or less the same (vide Table II, column 4). This shows that there is mutual influence in the mixture of *o*- and *p*-nitrophenols and, as shown above, the individual influences are of different magnitude.

Further, where the amount of *p*-nitrophenol is constant, the %influence of *para*- over *ortho* decreases with increasing amount of the latter. At the same time, it may be noted that *para*-nitrophenol being in large quantity, the influence exerted by it over the *ortho*-isomer will be of greater magnitude. Again, with increasing additions of *o*-nitrophenol, its %influence over the *para*-isomer, although of small magnitude, will increase at a certain rate. These two opposing influences would so adjust that a constant overall %influence is exhibited. Similarly, in the second reverse set of

experiments performed with a constant amount of *o*-nitrophenol and increasing amounts of *p*-nitrophenol, tht resultant %influence remains more or less constant, and is of the same order as above (vide Table II, column 8).

FIG. 3

Polarograms of mixtures o *&* p-*nitrophenols.*


Galvanometer Deflection in cms
pH 2·0
pH 2·0
pH 10·2
pH 10·2
O- 4 ml. of p - nitrophenol
+ 2 ml. of o - nitrophenol
O- 4 ml. of o - nitrophenol
+ 2 ml. of p - nitrophenol
E d.e. in Volts (vs. S.C.E.)

In view of the variations in the amounts of the two substances, the stability of H-bonding in *o*-nitrophenol may not be to the same extent in all the mixtures studied and also may not be of the same order as in *o*-nitrophenol molecule.

If the influence of *para-* over *ortho*-nitrophenol is viewed as resulting in the destabilisation of the H-bonding in the latter, the decreasing influence of *para-* over *ortho*-phenol (*vide supra*) would mean a gradual increase in the stability of *o*-nitrophenol, *i. e.*, the H-bonding is made more stable so that its contribution towards the observed wave-height decreases gradually, as the H-bonding is responsible for the decreased wave-height of *o*-nitrophenol as compared to that of the *p*-isomer (*vide supra*). Similarly, in the reverse set of mixtures, the %influence of *para-* over *ortho*-nitrophenol increases gradually and, hence, the H-bonding in the latter is made less and less stable.

If there were no mutual influence, one would expect a polarogram with a distinct double wave, since the difference in the half-wave potentials, viz. 0.27V (vide Table I), is sufficient enough to effect a separation of the waves. But the mutual influence resulting in overall %influence (*vide supra*) shows that they are reduced at the

electrode in such a way that the two waves, otherwise expected, coalesce, giving rise to a single wave as observed (vide Fig. 3). The polarograms are of similar pattern.

TABLE II

Polarographic study of mixtures of o- & p-*nitrophenols at* p_H 10.2 *and at* 2.0.

Amount of *p*-nitrophenol = 4 c.c.				Amount of *o*-nitrophenol = 4 c.c.			
Amount of *o*-nitrophenol.	$E_{\frac{1}{2}}$ (vs. S.C.E.).	Obs. i_D.	% Influence.	Amount of *p*-nitrophenol.	$E_{\frac{1}{2}}$ (vs. S.C.E.).	Obs. i_D.	% Influence.
			A. At p_H 10.2.				
0.5 c.c.	−0.999 volt	9.45 cm	19 6	0.5 c.c.	−0 730 volt	9.10 cm.	13.6 *
1.0	−0.970	10.00	22.5	1.0	−0.750	9.70	18.1
1.5	−0.935	10.80	23.1	1.5	−0.765	10.40	21.1
2.0	−0.970	11.90	21.7	2.0	−0.770	11.50	20.7
2.5	−0.88	12.30	24.5	2 5	−0.825	12.10	23.6
3.0	−0.880	13.30	24.0	3.0	−0.825	13.30	22.5
3.5	−0.870	13.80	26.0	3.5	−0.835	13.80	25.3
4.0	−0.880	14.80	25.3	4.0	−0 855	14.70	25.8
			Mean 23.4				Mean 22.4
			B. At p_H 2.0.				
0.5	−0.305	11.25	22.2*	0.5	−0.245	11.20	16.0*
1.0	−0.305	13.63	14.4	1.0	−0.255	12.00	19.7
1.5	−0.305	14.50	16.6	1.5	−0.260	12.70	23.4
2.0	−0.300	16.38	13.1	2.0	−0.280	13.80	24.2
2.5	−0.310	17.25	15.1	2.5	−0.280	14 70	25.9
3.0	−0.305	18.75	13.9	3.0	−0.290	14.90	30.5*
3.5	−0.300	15.25	34.4*	3.5	−0.290	15.80	31.5*
4.0	−0.310	18.25	26.1*	4.0	−0.310	18.25	26.1
			Mean 14.6				Mean 23.9

* Not considered in the evaluation of the mean %influence.

As seen from Table II-A, the half-wave potentials of the mixtures at p_H 10.2 vary gradually from a value corresponding to the substance in excess (cf. Table 1; $E_{\frac{1}{2}}$ for *ortho-* and *para* at p_H 10.2 are 0.720V and 0.990V respectively) with increasing amounts of the other. These values for the mixtures suggest that the nature of the mixture changes to a more reducible (vide Table II, column 2) or less reducible (Table II column 6), depending on the amount of *o*-nitrophenol present in the mixture.

Polarograms at p_H 2.0.—The polarograms of mixtures at p_H 2.0 consist of single waves (vide Fig. 3).

As at p_H 10.2, the observed wave-heights are always less than those calculated on the additivity principle. Thus, the mutual influence is exhibited at this p_H as well. Except in one or two mixtures, the %influence remains more or less the same (vide Table II-B) in each set of experiments, the deviations observed being attributed to experimental errors. The order of the %influence is different for the two sets of mixtures unlike at p_H 10.2. This difference is due to the effect of p_H. Also, in the mixtures consisting of 4 c.c. of *o*-nitrophenol and varying amounts of the *para*-isomer,

the %influence increases at a slow rate, unlike at p_H 10.2. This again is due to the acidic nature of the solution.

Regarding the variation of mutual influence in mixtures, the same explanation (vide p_H 10.2) holds good, *i. e.*, *o*-nitrophenol has got little influence over *p* nitropnenol and the latter possesses an appreciable influence over the *ortho*-isomer in destabilising the H-bonding.

The general characteristics of the polarograms at p_H 2.0 are the same as at p_H 10.2. Unlike at p_H 10.2, the mixtures at p_H 2.0 exhibit different behaviour. The half-wave potentials of mixtures with 4 c.c. of *p*-nitrophenol and varying amounts of *o*-isomer remain more or less the same, viz., −0.305V (vide Table II-B) *i. e.*, the mixtures exhibit a half-wave potential nearer to that of *p*-nitrophenol (−0.330V ; Table I-B, column 3), indicating thereby that the reducible character remains the same. In other words, *o*-nitrophenol influences the nature of the mixture to a very small extent.

In the reverse set of experiments (vide Table II-B) the half-wave potentials of the mixtrues increase gradually from a value nearer to that of *o*-nitrophenol alone (−0.205V, vide Table I-A) to a value approaching that of *p*-nitrophenol (−0.330V), *i. e.*, the nature of the mixture changes from one of an easily reducible to that of relatively difficultly reducible character.

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THIAZOLE DERIVATIVES AS ANTISPASMODICS AND ANTIHISTAMINICS. PART III

By Pranabandhu Tripathy, H. K. Pujari and M. K. Rout

Four different series of compounds, prepared by reacting 4-aryl-2-aminothiazoles with paraformaldehyde and one of the following: (*a*) a ketone (several ketones have been used), (*b*) 1-phenyl-3-methyl-5-pyrazolone, (*c*) 8-hydroxyquinoline and (*d*) diethylamine, have been studied for spasmolytic and antihistaminic action. The one formed with 2-aminotetrahydrobenzothiazole, paraformaldehyde and 1-phenyl-3-methyl-5-pyrazolone has proved most effective.

Of these, 4-aryl-2-(1-phenyl-3-methyl-5-keto-4-pyrazolinyl-)-methFlaminothiazoles have been found to possess significant antispasmodic and antihistaminic activities.

In view of the antispasmodic activity of certain substituted β-aminoalkylaryl ketones (Blicke, *Ann. Rev. Biochem.*, 1943, **13**, 549; Denton *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 2048), pyrazolone derivatives (Notkin and Webster, *Rev. Canadian Biol.*, 1942, **1**, 660; Pathak and Ghosh, this *Journal*, 1949, **26**, 371) and pyridyl- and thiazolyl-quinoline derivatives (Heilbron *et al.*, *J. Chem. Soc.*, 1949, 419), it was thought of interest to prepare in the present investigation some *p*-aminoketones with thiazolyl substituents attached to the secondary amino groups and also to synthesise thiazolyl-quinoline and thiazolyl- or benzothiazolyl-pyrazolone derivatives for use as antispasmodics. Thiazoles have been taken up for investigation as some thiazole derivatives described by Chance, Dirnhuber and Robinson are found to exhibit musculotropic activity (*Brit. J. Pharmacol.*, 1946, **1**, 153) and the presence of sulphur-containing groups like thiazolyl, thienyl etc. may promote antispasmodic activity, as indicated by the observation of Blicke and Taso (*J. Amer. Chem. Soc.*, 1944, **66**, 1645) and of Anderson and Green (*Nature*, 1950, **165**, 122).

Because of the observation of Erlenmeyer and Müller (*Helv. Chim. Acta*, 1945, **28**, 922), Sondern and Breivogel (U.S. Patent 2,440,730/1948), Dahlbon (*Acta Chem. Scand.*, 1950, **4**, 744) and Kaye and Parris (*J. Org. Chem.*, 1951, **16**, 1761), it was also proposed to test the above compounds as antihistaminics. Virtually all the antihistaminic compounds contain the structural unit $R_2N—C—C—X$ in which X is a group beginning with oxygen ($R_2N—C—C—O—$), nitrogen ($R_2N—C—C—N<$) or carbon ($R_2N—C—C—C<$). Therefore attempts were made to introduce the latter group into thiazole nucleus by condensing it with paraformaldehyde and ketones or ketomethylene compounds with the hope of synthesising possible efficient antihistaminics.

Condensation of thiazole compounds with quinoline or pyrazolone would also help to study how the attachment of an additional therapeutically active quinoline or pyrazolone nucleus adds to the importance of thiazoles in therapy, particularly as antispasmodics and antihistaminics.

In the present investigation 4-phenyl-, 4-*p*-hydroxy-*m*-methoxyphenyl-, 4-phenylethyl-, and 4-β-naphthyl-2-aminothiazoles have been prepared by the method of Dodson and King (*J. Amer. Chem. Soc.*, 1945, **67**, 2243). These thiazoles have been condensed with different ketones and formaldehyde.

Similarly, three other series of thiazole derivatives have also been prepared by substituting one of the following: (*a*) 1-phenyl-3-methyl-5-pyrazolone, (*b*) 8-hydroxyquinoline and (*c*) diethylamine, for ketones in the synthesis of the first series.

All these four series of thiazole derivatives have been screened for their antispasmodic and antihistaminic action in the S.C.B. Medical College, Cuttack, Orissa, under the supervision of Dr. J. K. Mohanty.

Of all the compounds reported in this paper, compounds III, VII, XVII have been found to possess pronounced antihistaminic as well as antispasmodic activity. Particularly compound III has been found to exhibit third of the activity of antazoline hydrochloride.

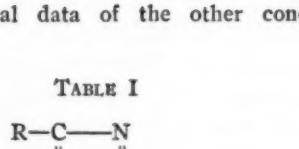
Compounds VIII and X also possess antispasmodic action in concentrations varying from 2×10^{-5} to 2×10^{-6}. Detailed procedure and results of these will be published elsewhere.

EXPERIMENTAL

Condensation of 4-Phenyl-2-aminothiazole with Formaldehyde and Acetophenone (I).—A mixture of 4-phenyl-2-aminothiazole (1.76 g.), acetophenone (1.2 g.) and paraformaldehyde (0.9 g.) in HCl (conc., 3 c.c.) and alcohol (25 c.c.) was heated under reflux for 2 hours. An additional amount of paraformaldehyde (0.6 g.) was then added and refluxing continued for 3 hours more. The alcohol was distilled off when a pasty mass was obtained which on keeping in contact with ammonia for 2 to 3 hours solidified. It was washed well with water and recrystallised from alcohol, m.p. 115°, yield 82%. (Found: N, 9.0; S, 9.98. $C_{18}H_{16}ON_2S$ requires N, 9.09; S, 10.39%).

The properties and analytical data of the other condensation products are recorded in Table I.

TABLE I



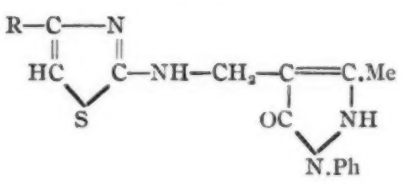
Comp. No.	R=	R'=	Yield.	M.P.	% Nitrogen. Found.	% Nitrogen. Calc.	% Sulphur. Found.	% Sulphur. Calc.
VI	C_6H_5-	-$CH_2CH_2COC_6H_4OH(p)$	88%	78°	8.20	8.28	9.25	9.47
VII	C_6H_5-	-$CH_2COC_6H_4OH(p)$	72	89°	8.40	8.64	9.62	9.88
VIII	C_6H_5-	-$CH_2COCH{=}CHC_6H_5$	75	130°	8.20	8.38	9.40	9.58
IX	C_6H_5-	-CH_2CO-$C_6H_3(OCH_3)OH(p)$	85	81°	7.92	8.09	9.64	9.25
X	C_6H_5-	-$CH_2COC_6H_4OCH_3(p)$	75	86°	8.10	8.28	9.10	9.47
XI	$C_6H_5CH_2CH_2$-	-$CH_2COC_6H_5$	80	145°	8.50	8.34	9.60	9.52
XII	$(p)HOC_6H_4$-	-$CH_2COC_6H_5$	70	180°(d)	8.85	8.64	9.95	9.88
XIII	$(p)HOC_6H_3(OCH_3)(m)$-	-$CH_2COC_6H_5$	75	160°(d)	8.12	8.09	9.80	9.25
XIV	β-$C_{10}H_7$	-$CH_2COC_6H_5$	70	132°	7.70	7.82	8.70	8.94

4-Phenyl-2-(1′-phenyl-3′-methyl-5′-keto-4′-pyrazolinyl)-methylamino thiazole (II).—A mixture consisting of 1-phenyl-3-methyl-5-pyrazolone (1.73 g.) (prepared by the method described in "Quantitative Organic Analysis" By Vogel), paraformaldehyde (1.2 g.) and 4-phenyl-2-aminothiazole (1.76 g.) in HCl (conc., 3 c.c.) and alcohol (25 c.c.) was refluxed over an asbestos-wire gauge for 8 hours. After reflux the alcohol was distilled off and the mass was poured into a large volume of water. The gummy product, thus obtained, hardened up in contact with ammonia (conc.). It was purified by dissolving in NaOH and reprecipitating with acetic acid, m.p. 121°, yield 85%. (Found: N, 15.3; S, 8.9. $C_{20}H_{18}ON_4S$ requires N, 15.47; S, 8.84%).

Condensation of 2-Amino-4:5:6:7-tetrahydrobenzothiazole with 1-Phenyl-3-methylpyrazolone (III).—A mixture of 1-phenyl-3-methylpyrazolone (1.73 g.), 2-amino-4:5:6:7-tetrahydrobenzothiazole (2.3 g.) and paraformaldehyde (1.2 g.) in HCl (conc., 3 c.c.) and alcohol (20 c.c.) was refluxed for 8 hours. The compound was separated and purified as above, m.p. 102° (decomp.), yield 82%. (Found: N, 16.3; S, 9.6. $C_{18}H_{21}ON_4S$ requires N, 16.4; S, 9.4%).

The properties and analytical data of the different condensation products are described in Table II.

TABLE II



Comp. No.	R=	Yield.	M.P.	% Nitrogen. Found.	% Nitrogen. Calc.	% Sulphur. Found.	% Sulphur. Calc.
XV	(*p*) HO, (*m*)H_3CO C_6H_3	78%	180°(d)	13.60	13.73	7.80	7.84
XVI	$C_6H_5CH_2CH_2$-	80	145-46°	14.30	14.32	9.10	8.20
XVII	(*p*)HO.C_6H_4-	65	160°(d)	14.44	14.51	8.10	8.47
XVIII	β-$C_{10}H_7$-	85	158°	13.70	13.59	7.90	7.77

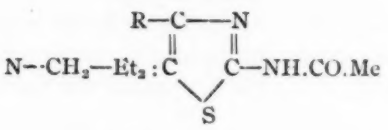
4-Phenyl-2-(8′-hydroxy-7′-quinolinyl)-methylaminothiazole (IV).—A mixture of 8-hydroxyquinoline (1.76 g.), 4-phenyl-2-aminothiazole (1.76 g.) and paraformaldehyde (1.2 g.) in HCl (conc., 3 c.c.) and alcohol (25 c.c.) was heated under reflux, and the desired product was isolated in the same manner as described above, m.p. 101°, yield 65%. (Found: N, 12.8; S, 10.0. $C_{19}H_{15}ON_3S$ requires N, 12.61; S, 9.6%).

2-Acetamido-4-phenyl-5-diethylaminomethylthiazole (V).—2-Acetamido-4-phenylthiazole (2.1 g.) (obtained by acetylating 2-amino 4-phenylthiazole) was taken and to it diethylamine (0.6 g.) in acetic acid (5 c.c.) and formalin (1 c.c.) were added. The reaction mixture was refluxed for 8 hours on a water-bath. After heating, it was diluted with 10 c.c. of water and was then treated with a saturated solution of K_2CO_3 solution. The precipitate, thus obtained, was filtered, washed well with water

and finally recrystallised from alcohol, and dried in a vacuum desiccator, m.p. 80°, yield 75%. (Found : N, 14.02 ; S, 10.38. $C_{16}H_{21}ON_3S$ requires N, 13.87 ; S, 10.56%).

The properties and analytical data of the other condensation products are illustrated in Table III.

TABLE III



Comp. No.	R=	Yield.	M.P.	% Nitrogen. Found.	% Nitrogen. Calc.	% Sulphur. Found.	% Sulphur. Calc.
XIX	$C_6H_5CH_2CH_2$-	80%	188° (d)	12.70	12.69	9.60	9.67
XX	β-$C_{10}H_7$[a]	85	245° (d)	11.78	11.90	8.70	9.06

The authors are grateful to the Board of Scientific and Industrial Research, Orissa, for research grants to carry out this investigation and to Dr. J. K. Mohanty, Assistant Prof. of Pharmacology, Orissa Medical College, for help in carrying out these tests.

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ACTION OF NITROGEN DIOXIDE AND ITS DISSOCIATION PRODUCTS ON NITRITES OF SODIUM, POTASSIUM AND SILVER

By Vasantrai Trambaklal Oza

The action of nitrogen dioxide and its thermal dissociation products has been studied at about 130° and at temperatures above 130° for half an hour on $AgNO_2$, KNO_2 and $NaNO_2$. Only $AgNO_2$ reacts appreciably at 130°; the anhydrous nitrites, stable at 130°, are found not to react at this temperature. KNO_2 reacts at 140°, and $NaNO_2$ at 200°; the reaction is maximum at 200° in the case of KNO_2 and at 250° in the case of $NaNO_2$; in either case the reaction diminishes thereafter.

The action of nitrogen dioxide on silver nitrite was studied by Divers and Schimidzu (*J. Chem. Soc.*, 1885, **47**, 630) who found no action between the two. Ostwald (*Ann. chim.*, 1914, *ix*, **1**, 44) found that nitrites underwent oxidation by nitrogen tetroxide and nitrogen dioxide below 100°, while Partington and Williams (*J. Chem. Soc.*, 1924, 947) found that above 180° nitrites became oxidised to nitrate. Addison and Lewis (*ibid.*, 1953, 1874) were of the opinion that nitrites underwent little change in contact with nitrogen tetroxide and its thermal dissociation products up to 130°.

The present work was planned to study the action of nitrogen dioxide and its thermal dissociation products formed above 130° on anhydrous nitrites. The results of the present work show that the reaction is dependent also on the nature of the nitrite.

Experimental

Sodium nitrite used was the pure salt, recrystallised and analysed for purity. Potassium nitrite was the same as that prepared by Oza and Walawalkar (this *Journal*, 1943, **20**, 315). Silver nitrite was the same as used by Oza, Oza and Thaker (*J. Chem. Soc.*, 1955, 2457).

The experimental technique and apparatus were the same as described by Oza, Oza and Thaker (*loc. cit.*). The results recorded in Table I show that (*i*) in the case of $NaNO_2$ and KNO_2, the amount of N_2O_3 formed is very nearly equal to the amount of N_2O_4 consumed; (*ii*) except with $AgNO_2$, which begins to decompose at 128° (Oza, Oza and Thaker, *loc. cit.*), all the nitrite consumed is quantitatively oxidised to nitrate; (*iii*) with KNO_2 there is no reaction at 130°, but considerable one at 140°, while with $NaNO_2$ no reaction is observed even at 150°, and there is about 10% reaction at 200°; again, with KNO_2 the reaction is maximum at 200° and with $NaNO_2$ it is maximum at 250°, as above these temperatures the extent of the reaction is found to diminish; (*iv*) as distinguished from the behaviour of KNO_2 and $NaNO_2$, as pointed out under (*i*) and (*ii*), silver nitrite does not form its equivalent nitrate, evidently because a part of it decomposes: more nitric oxide ($\equiv$ of N_2O_3) is formed than expected if the behaviour were similar to KNO_2 and $NaNO_2$ while silver metal makes its appearance.

TABLE I

(a) System: $NaNO_2 + NO_2$.

Expt. No.	Temp.	Substance taken. (g.)	N_2O_4 taken. (g.)	Substance consumed. (g.)	Nitrate formed. (g.)	Metal formed. (g.)	N_2O_4 left. (c.c.)	N_2O_4 consumed. (c.c.)	N_2O_3 formed. (c.c.)	Approx ratios. 5:9.	5:6.	5:10.	9:10.
1.	150°	0.2220	0.1710	...	...	...	41.5	...	...	...	...	...	...
2.	200°	0.2270	0.2355 (57.34)	0.0230 (3.35×10^{-4})	0.02845 (3.35×10^{-4})	...	51.2	6.14 (2.7×10^{-4})	6.2 (2.77×10^{-4})	1	1	1	1
3.	250°	0.1044	0.2250 (54.9)	0.07196 (10.4×10^{-4})	0.8860 (10.4×10^{-4})	...	32.3	22.6 (10.01×10^{-4})	22.4 (10.0×10^{-4})	1	1	1	1
4.	300°	0.1204	0.2850 (69.4)	0.0615 (8.9×10^{-4})	0.0758 (8.9×10^{-4})	...	49.2	22.5 (9.0×10^{-4})	22.0 (8.99×10^{-4})	1	1	1	1
5.	350°	0.1000	0.2240 (54.5)	0.0457 (6.6×10^{-4})	0.0563 (6.6×10^{-4})	...	39.7	14.8 (6.6×10^{-4})	14.0 (6.67×10^{-4})	1	1	1	1
(b)	System: $KNO_2 + NO_2$.												
6.	130°	0.1001	0.2754	...	...	...	...	...	...	...	...	...	...
7.	140°	0.1032	0.2810 (68.3)	0.05844 (6.87×10^{-4})	0.06944 (6.87×10^{-4})	...	52.9	15.4 (6.87×10^{-4})	15.62 (6.97×10^{-4})	1	1	1	1
8.	200°	0.1040	0.2110 (51.37)	0.0800 (9.41×10^{-4})	0.0950 (9.41×10^{-4})	...	30.37	21.0 (9.37×10^{-4})	21.2 (9.4×10^{-4})	1	1	1	1
9.	250°	0.1010	0.2374 (57.85)	0.06956 (8.18×10^{-4})	0.08256 (8.17×10^{-4})	...	39.65	18.2 (8.1×10^{-4})	18.5 (8.2×10^{-4})	1	1	1	1
10.	300°	0.1020	0.2390 (58.2)	0.06374 (7.5×10^{-4})	0.07574 (7.5×10^{-4})	...	41.8	16.4 (7.32×10^{-4})	16.6 (7.4×10^{-4})	1	1	1	1
11.	350°	0.1018	0.2194 (53.4)	0.05312 (6.25×10^{-4})	0.06312 (6.25×10^{-4})	...	39.4	14.0 (6.25×10^{-4})	14.2 (6.345×10^{-4})	1	1	1	1
* (c)	System: $AgNO_2 + NO_2$												
12.	130°	0.2660	0.148 (36.04)	0.0405 (2.63×10^{-4})	0.0326 (2.13×10^{-4})	0.0043 (0.4×10^{-4})	27.8	8.24 (3.67×10^{-4})	8.82 (3.69×10^{-4})	0.72	1.2	0.67	0.94
13.	200°	0.2060	0.2650 (64.5)	0.1449 (9.4×10^{-4})	0.0916 (5.5×10^{-4})	0.04234 (3.9×10^{-4})	56.88	7.62 (3.4×10^{-4})	12.00 (5.3×10^{-4})	1.2	1.7	1.8	0.64

* These results are reproduced from Oza, Oza and Thaker (*loc. cit.*).

Discussion

From these results it appears possible to infer that some anhydrous nitrites can react with nitrogen dioxide round about 130°. The temperature of the bath may be the temperature of the nitrite, but will not be the temperature of the gas, as a part of the system outside the bath is exposed to air. The overall temperature of the gas will therefore be less than those recorded in the table. At 140°, the molecular species of the nitrogen oxide is almost all NO_2 (Richardson, *J. Chem. Soc.*, 1887, **51**, 397) and this temperature is probably slightly higher (Addison and Lewis, *loc. cit.*). Hence, it appears that the nitrites might undergo oxidation at 130-140° as

$$MNO_2 + NO_2 \longrightarrow MNO_3 + NO \qquad \ldots (i)$$

forming nitrate and nitric oxide, as found in these experiments in the case of silver nitrite. This oxidation is found to occur not uniformly at 130-40°, and is therefore dependent on the nature of the nitrite.

Silver nitrite is oxidised at 130°. Although this substance is now known to commence decomposing at 128°, forming silver oxide, nitric oxide and nitrogen dioxide, and silver oxide to react with nitrogen dioxide (cf. Oza, Oza and Thaker, *loc. cit.*) as

$$Ag_2O + NO_2 \longrightarrow AgNO_3 + Ag,$$

the experimental results show unmistakably that this contributes but very little to the formation of nitrate found at 130° ; for Ag found and nitric oxide found in excess of the requirement of (*i*), are not very large at this temperature. At higher temperatures, these influences do play a part in the case of silver nitrite as there is no other way of explaining the large amount of nitric oxide formed, since Ag_2O reacts with NO_2 without forming nitric oxide (Oza, Oza and Thaker, *loc. cit.*) : Silver is actually large at 200°.

In the case of sodium and potassium nitrites, the reaction (*i*) is found to occur at temperatures higher than 130° ; further, the temperature is higher with sodium nitrite than with potassium nitrite. As a matter of fact, potassium nitrite fuses and decomposes at a higher temperature than sodium nitrite does (Oza, this *Journal*, 1945, **22**, 173). This shows that the reaction of nitrogen dioxide, forming nitrites, is not dependent on the prior decomposition of nitrite—an inference not unlikely from the behaviour of silver nitrite.

The only remaining observation of this work is the inversion in the course of oxidation of nitrite which occurs after a certain temperature with sodium and potassium nitrites. This must be ascribed to the effect of nitric oxide, increasingly formed, with rise of temperature, from NO_2 (as $NO_2 \longrightarrow NO + \frac{1}{2} O_2$) and also as in (*i*) above, on nitrate as

$$MNO_3 + NO \longrightarrow MNO_2 + NO_2 \qquad \ldots (ii)$$

The reaction (*ii*) becomes prominent with rise in temperature (Oza, Oza and Thaker, *loc. cit.*).

The present work shows that nitrate found in the oxidation products of nitrite by nitrogen dioxide is the result of the reversible reaction (Oza and Oza, *J. Chem. Soc.*, 1953, 907 ; Oza, Oza and Thaker, *loc. cit.*) :

$$MNO_2 + NO_2 \rightleftharpoons MNO_3 + NO$$

If the nitrite is not stable at the temperature of the experiment, some of it may also be formed as :

$$M_2O + NO_2 \rightarrow MNO_3 + M.$$

Above 130-40°, NO_2 is known to dissociate as $NO_2 \rightleftharpoons NO + \frac{1}{2} O_2$ (Bodenstein and Kotayama, *Z. Electrochem.*, 1909, **15**, 244), and it appears that the oxygen, so formed, may have but little effect in bringing about oxidation of the nitrite. The work of Johnston and Walker (*J. Amer. Chem. Soc.*, 1933, **55**, 172) shows that the concentration of atomic oxygen at such a temperature will be exceedingly small and negligible.

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AMINO DERIVATIVES OF TITANIUM TETRABROMIDE. PART IV

By Sarju Prasad and Jai Beniprasad Tripathi

The amino derivatives of titanium tetrabromide have been prepared by the action of titanium tetrabromide on some aliphatic and aromatic amines, and their properties studied.

In earlier communications of the series (this *Journal*, 1956, **33**, 838; 1957, **34**, 152), the action of titanium tetrabromide on some amines and heterocyclic bases was studied. The work has now been extended to the study of the effect of some less common amines having one or more :NH or ⋮N groups on anhydrous titanic bromide.

Experimental

The amines used were of Merck's or B.D.H.'s 'extra pure' quality. Titanium tetrabromide was prepared by the method of Olsen and Ryan (*J. Amer. Chem. Soc.*, 1932, **54**, 2215), redistilled at 230° and extracted with anhydrous ether, distilled over sodium metal.

General Method of Preparation.—The compounds were prepared by adding slowly a dilute ethereal solution of titanic bromide to amine solution in ether with constant shaking. However, if the process be reversed, a sticky mass is generally obtained which is not easily converted into a pure crystalline precipitate. The precipitate formed was stirred well with a slight excess of the amine solution and kept for about ½ hour in a dry atmosphere; it was filtered and washed with ether till free of the amine. It was dried over anhydrous calcium chloride, analysed and the properties studied. In the compounds: *tetrakis*-*n*-butylanilino-, -*n*-propylanilino-, *iso*-amylanilino-, -dimethyl-*o*-toluidino-, -diethyl-*o*-toluidino-, -dimethyl-*p*-toluidino-, and -diethyl-*p*-toluidino-titanic bromides, the amines were also estimated by the potentiometric method. Duplicate titrations were carried out. The results recorded in Table II are the averages of the two values.

Estimation of Amine.—The compound (~0.2-0.8 g.) was weighed out accurately, treated with HCl (50 c.c., conc.) and the volume made up to 250 c.c. An aliquot of the solution (25 c.c.) was pipetted out in an iodine flask and 15 c.c. each of $M/2$-KBr and 0.1N-$KBrO_3$ added to it. It was kept for a definite period of time (vide Table I) and 15 c.c. of 0.1N-As_2O_3 added to it. The mixture was shaken well, filtered in case any precipitate or turbidity appeared, and titrated back with $KBrO_3$ at the room temperature. The curves (vol. of $KBrO_3$ in c.c. against $\Delta E/\Delta V$) were drawn and from the amount of bromine consumed, the quantity of amine and the percentage of nitrogen in the compounds calculated.

The blank titrations were carried out with each amine under identical conditions. Only the curves for *iso*amylaniline and diethyl-*p*-toluidine (Fig. 1, curves I & II) have been shown.

FIG. 1

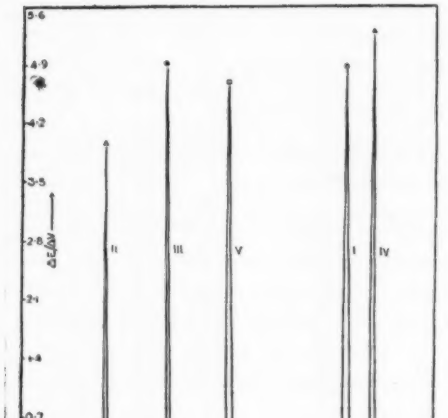
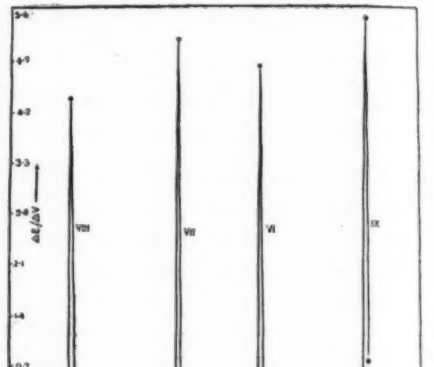


FIG. 2



The curves III-V in Fig. 1 and VI-IX in Fig. 2 refer to the estimation of amine in *tetrakis*-diethyl-*o*-toluidino-, -dimethyl-*p*-toluidino-, -diethyl-*p*-toluidino-, -*n*-propylanilino-, -*n*-butylanilino-, *iso*amylanilino-, and dimethyl-*o*-toluidino-titanic bromide respectively.

TABLE I

Amines.	Wt. in 100 c.c.	Bromination period.	Bromine consumed.
n-Propylaniline	0.3378 g.	2-5 mins.	$3Br_2$
n-Butylaniline	0.1756	,,	$3Br_2$
*iso*Amylaniline	0.1838	,,	$3Br_2$
Dimethyl-*o*-toluidine	0.1734	25-30	$2Br_2$
Diethyl-*o*- ,,	0.2026	,,	$1Br_2$
Dimethyl-*p*- ,,	0.4182	,,	$1Br_2$
Diethyl-*p*- ,,	0.5118	,,	$1Br_2$

TABLE II*

Compounds.	Wt. of the compound.	Wt. of the amine. Calc.	Found (from the curve).	% Nitrogen.
*iso*Amylaniline	0.1838 g.	0.1838 g.	0.1840 g.	8.60
Diethyl-*o*-toluidine	0.2026	0.2026	0.2011	8.52
t-*n*-Propylanilino-T.B.	0.4318	0.2568	0.2558	6.17
t-*n*-Butylanilino-T.B.	0.3914	0.2420	0.2406	5.78
t-*iso*Amylanilino-T.B.	0.3196	0.2043	0.2033	5.46
t-Dimethyl-*o*-toluidino-T.B.	0.7698	0.4578	0.4566	6.15
t-Diethyl-*o*- ,,	0.4604	0.2943	0.2931	5.47
t-Dimethyl-*p*- ,,	0.8206	0.4880	0.4909	6.20
t-Diethyl-*p*- ,,	0.5968	0.3815	0.3829	5.51

* *t* denotes tetrakis.
T.B. denotes tetanicbromide.

TABLE III

Compounds of titanium tetrabromide with secondary amines.

Amine.	Compound formed.	Colour.	M.P.	% Titanium. Found.	Calc.	% Bromine. Found.	Calc.	% Nitrogen. Found.	Calc.
n-Propyl-aniline	*t*-*n*-Propylanilino-T.B. $[Ti(C_6H_5.NHC_3H_7)_4]Br_4$	Brownish grey	108°	5.32	5.29	35.06	35.24	6.12	6.19
n-Butyl-aniline	*t*-*n*-Butylanilino-T.B. $[Ti(C_6H_5NH.C_4H_9)_4]Br_4$	White with greyish shade	97°	5.01	4.98	33.18	33.20	5.76	5.81
*iso*Amyl-aniline	*t*-*iso*Amylanilino-T.B $[Ti\{C_6H_5NH.C_3H_5(CH_3)_2\}_4]Br_4$	Dirty white	144°	4.70	4.71	31.26	31.37	5.42	5.49
Dibenzyl-amine	*t*-Dibenzylamino-T.B. $[Ti\{(C_6H_5CH_2)_2NH\}_4]Br_4$	White	...	4.11	4.15	27.58	27.68	4.80	4 84
Di-*p*-tolyl-amine	*t*-Di-*p*-tolylamino-T.B. $[Ti\{(CH_3C_6H_4)_2NH\}_4]Br_4$	Greyish white	182-83°	4.17	4.15	27.54	27.68	4.78	4.84
Di-*n*-propyl-amine	*t*-Di-*n*-propylamino-T.B. $(Ti\{(C_3H_7)_2NH\}_4]Br_4$	White	320°	6.20	6.22	41.37	41.45	7.16	7.25
Dimethyl-*p*-pheny-lene-diamine	*bis*-Dimethyl-*p*-phenylene-diamino-T.B. $[Ti\{C_6H_4(NH.CH_3)_2\}_4]Br_4$	Dark ash	...	7.52	7.50	49.8	50.00	8.68	8.75

TABLE IV

Compounds of titanium tetrabromide with tertiary amines.

Amine.	Compound formed.	Colour.	M.P.	% Titanium. Found.	Calc.	% Bromine. Found.	Calc.	% Nitrogen. Found.	Calc.
Dimethyl-*o*-toluidine	*t*-Dimethyl-*o*-toluidino-T.B. $[Ti\{CH_3C_6H_4N(CH_3)_2\}_4]Br_4$	Pinkish grey	86°	5.26	5.29	35.08	35.24	6.12	6.19
Diethyl-*o*-toluidine	*t*-Diethyl-*o*-toluidino-T.B. $[Ti\{CH_3.C_6H_4N(C_2H_5)_2\}_4]Br_4$	Greyish white	90°	4.72	4.71	31.24	31.37	5.41	5.49
Dimethyl-*p*-toluidine	*t*-Dimethyl-*p*-toluidino-T.B. $[Ti\{CH_3\ C_6H_4N(CH_3)_2\}_4]Br_4$	Yellow	78°	5 28	5.29	35.06	35.24	6.10	6.19
Diethyl-*p*-toluidine	*t*-Diethyl-*p*-toluidino-T.B. $[Ti\{CH_3.C_6H_4N(C_2H_5)_2\}_4]Br_4$	Dirty white	156°	4.69	4.71	31.28	31.37	5.44	5.49
Triethyl-amine	*t*-Triethylamino-T.B. $[Ti\{(C_2H_5)_3N\}_4]Br_4$	,,	309-10°	6.24	6.22	41.36	41.45	7.18	7.25
γ-Picoline	*t*-γ-Picolino-T.B. $[Ti(CH_3.C_5H_4.N)_4]Br_4$	White	212°	6.25	6.49	43.06	43.24	7.48	7.57
Tribenzyl-amine	*t*-Tribenzylamino-T.B. $[Ti\{(C_6H_5CH_2)_3N\}_4]Br_4$	,,	214°	3.19	3.17	21.06	21.11	3.65	3.69
**pp'*-Tetra-methyl-diamino-benzophe-none.	*bis*-*pp'*-Tetramethyl-diaminobenzophenone-T.B. $[Ti\{(CH_3)_2N.C_6H_4)_2CO\}_2]Br_4$	Orange-yellow	...	5.22	5.31	34.68	35.40	6.04	6.19

* Slightly low values were obtained as the compound was very hygroscopic in nature.

The compounds are insoluble in common organic solvents and are similar to the amino derivatives of titanium tetrabronide of the previous series. *tetrakis*-Dimethyl-*p*-toluidino-, -di-*n*-propylamino-, -di-*p*-tolylamino-, -triethylamino-, -γ-picolino-, and *bis*-*pp'*-tetramethyldiaminobenzophenone-titanic bromides are readily soluble in dilute mineral acids and the rest are insoluble. These hydrolyse slowly with cold water but readily with alkalies, and $Ti(OH)_4$ is precipitated according to the equation:

$$Ti\,(4A)\,Br_4 + 4NaOH \rightarrow Ti(OH)_4 + 4NaBr + 4A$$

(where A stands for the amine).

On heating with sodalime, the corresponding amine separates out like the other amino derivatives of the series. The compounds formed with tertiary amines are not so stable as those formed with primary or secondary amines. The compound, *bis*-*pp'*-tetramethyldiaminobenzophenone-titanic bromide, where the co-ordination through two tertiary nitrogen takes place, is extremely hygroscopic and decomposes when exposed to atmosphere. The compound, *bis*-dimethyl-*p*-phenylenediamino-titanic bromide, like the primary diamino derivatives, as shown in Part I (*loc. cit.*), is very stable. The stability may likewise be attributed to the formation of the chelate compound.

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SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT MATALS IN AQUEOUS SOLUTION. PART VII. MANGANESE ACETATO COMPLEXES

By S. K. Siddhanta and S. N. Banerjee

The p_H values of aqueous solution mixtures of manganese acetate and hydrochloric acid at different concentrations, after attainment of equilibrium, have been determined and the data obtained have been utilised to calculate the mass action constants, k_1 and k_2, for the two successive equilibria $MnAc_2 \rightleftharpoons MnAc^+ + Ac^-$ and $MnAc^+ \rightleftharpoons Mn^{2+} + Ac^-$, applying Bjerrum's method. The inapplicability of the method (modification of Bjerrum's method) of Siddhanta and Banerjee (Part III, this *Journal*, 1958, 35, 323) has been accounted for and a method has been suggested to calculate the values of thermodynamic dissociation constants, K_1 and K_2, from the values of the mass action constants determined above, by the direct application of "law of mass action", taking into accuont the activity coefficients of the individual ion, calculated from the ionic strength of the above solution mixture, employing the "Debye-Hückel limiting law".

Manganese acetate dissociates in aqueous solution in two stages :

$$MnAc_2 \rightleftharpoons MnAc^+ + Ac^- \quad \ldots (A)$$

$$MnAc^+ \rightleftharpoons Mn^{2+} + Ac^- \quad \ldots (B)$$

In the present paper the thermodynamic equilibrium constants, 'K_1' and 'K_2' (vide equations 1 and 2), have been found out from the determination of p_H of the solution mixtures of manganese acetate and hydrochloric acid by following a similar (but not identical) procedure as adopted in Parts III and V of this series (this *Journal*, 1958, 35, 323, 343).

$$K_1 = \frac{a_{MnAc^+} . a_{Ac^-}}{a_{MnAc_2}} = k_1 . \frac{f_{MnAc^+} . f_{Ac^-}}{f_{MnAc_2}} \quad \ldots (1)$$

and

$$K_2 = \frac{a_{Mn^{2+}} . a_{Ac^-}}{a_{MnAc^+}} = k_2 . \frac{f_{Mn^{2+}} . f_{Ac^-}}{f_{MnAc^+}} \quad \ldots (2)$$

where 'k_1' and 'k_2' are the classical concentration constants given by

$$k_1 = \frac{c_{MnAc^+} . c_{Ac^-}}{c_{MnAc_2}} \quad \text{and} \quad \ldots (3)$$

$$k_2 = \frac{c_{Mn^{2+}} . c_{Ac^-}}{c_{MnAc^+}} . \quad \ldots (4)$$

The values of 'k_1' and 'k_2' were found out by the graphical solution of the equation (5b), given in Part III (*loc. cit.*) as in the case of lead acetato complex. These values of 'k_1' and 'k_2' were utilised to find out the ionic strength, 'μ', and the activity coefficients, 'f_1' and 'f_2', for monovalent and divalent ions respectively, the procedure being identical as that adopted for lead acetate, referred to above.

Unfortunately, in the case of manganese acetate, comparatively high concentration of the salt had to be used for the sake of accuracy in calculating 'a_{H^+}' from p_H values. As a result of using higher concentrations of manganese acetate, as also of its greater dissociation, the ionic strengths of the mixtures used rose high, and in the regions where 'μ' was somewhat lower, recalculated value of 'x' approached '$2C$' quite closely, so that '$2C-x$' was erroneous. In the cases of lead acetate and lead propionate (Part III, *loc. cit.*) and cobalt acetate (Part V, *loc. cit.*), however, solution mixtures with values of 'μ' less than 0.05 in most cases could be used without prejudice to the value of 'a_{H^+}' in spite of the experimental error in the p_H determinations. Since the ionic strength was low, the value of 'f_1' obtained was reasonably accurate and the value of 'x' calculated, using this value of 'f_1', contained relatively small error and, hence, the relative error in "$2C-x$" was also small. Moreover, the dissociation was such that "$2C-x$" was substantially greater than zero for the solution mixtures used. Manganese acetate, however, has a much larger degree of dissociation, leading naturally to a small value of "$2C-x$", and if "$2C-x$" is determined by the procedure followed for lead acetate, it will contain larger relative error arising from the inaccuracy of the value of 'f_1' used. Therefore in the case of manganese acetate, the functions

$$c_{Ac^-}{}^2 \frac{x}{2C-x} \cdot f_1{}^2 f_2 \text{ and } c_{Ac^-} \cdot \frac{C-x}{2C-x} \cdot f_2$$

could not be calculated with sufficient accuracy, and as such the graphical solution of equation (5C) (Part III, *loc. cit.*) was not possible in this case.

The constants K_1 and K_2 were, however, determined by the direct application of equations (1) and (2) in the forms (1a) and (2a) respectively.

$$K_1 = \frac{c_{MnAc^+} \cdot c_{Ac^-}}{c_{MnAc_2}} \cdot f_1{}^2 \quad \ldots \quad \ldots \quad (1a)$$

(f_{MnAc_2} being equal to 1, since, $MnAc_2$ is a non-electrolyte) and

$$K_2 = \frac{c_{Mn^{2+}} \cdot c_{Ac^-}}{c_{MnAc^+}} \cdot f_2 \quad \ldots \quad \ldots \quad (2a)$$

In these calculations the values of '$c_{Mn^{2+}}$', 'c_{MnAc^+}', 'f_1' and 'f_2' already found, as indicated above from the approximate value of k_2 ($k_2 = 50 \times 10^{-3}$), have been used*; c_{MnAc_2} has been calculated from equation (5).

$$C = c_{MnAc_2} + c_{MnAc^+} + c_{Mn^{2+}} \quad \ldots \quad \ldots \quad (5)$$

This value, however, involves errors in both '$c_{Mn^{2+}}$' and 'c_{MnAc^+}' and, hence, is not so accurate; the relative error in 'c_{MnAc_2}' becomes larger and larger as "$c_{Mn^{2+}} + c_{MnAc^+}$" approaches 'C'. For this reason, the values of 'K_1' obtained are not at all accurate and are only indicative of the order. By averaging all the values of 'K_1', obtained in the above way, we get $K_1 = 1.43 \times 10^{-1}$ at room temperature. The individual values of 'K_1' are erratic, apparently showing no dependence on ionic strengths for the respective solution mixtures.

* Values of '$c_{Ac^-}{}^2$', recalculated by the equation $c_{Ac^-} = \frac{K_a C_a}{a_{H^+} f_1}$ have been used.

The values of 'K_2' obtained, however, become progressively lower at higher ionic strength, showing the dependence of K_2', so calculated, on the respective ionic strengths, evidently due to the inapplicability of the "Debye Hückel limiting law" to solutions of finite ionic strength, as has already been explained in detail in the case of lead acetate (this *Journal*, 1958, **35**, 269). The pK_2 values corresponding to those of 'K_2', obtained in this paper, are plotted against the respective values of $\sqrt{\mu}$ in the graph, obtained for manganese chloride and acetic acid mixtures, shown in Fig. 2 in Part VI (*ibid.*, 1958, **35**, 349), and these points (represented by □ mark) have been found to lie on the same straight line curve representing $pK/\sqrt{\mu}$ plot of the above paper. The value of the thermodynamic constant 'K_2' is therefore the same as that obtained in Part VI (*loc. cit.*), and it is $K_2 = 60.3 \times 10^{-3}$ at room temperature.

There appears to be no previous work on the determination of these constants in the case of manganese acetate.

TABLE I

The symbols used in the table headings and their evaluations are same as in Part III (*loc.cit.*).

Soln. No.	C*.	C_a*.	$t°$.	p_H.	$a_{A^-}{}^2 \times 10^3$ ($K_a = 1.80 \times 10^{-5}$).	a_{A^-}. $\frac{C-x}{2C-x} \times 10^3$.	$a_{A^-}{}^2 \frac{x}{2C-x} \times 10^3$.
1	0.025	0.020	28.8°	4.758	20.62	−34.48	1.84
2	0.035	,,	,,	4.955	32.46	−32.39	3.16
3	0.040	,,	,,	5.04	39.47	−37.43	4.51
4	0.045	,,	,,	5.07	42.31	−26.34	4.02
5	0.050	,,	,,	5.12	47.43	−25.38	4.66
6	0.055	,,	,,	5.16	52.02	−23.30	5.13
7	0.060	,,	,,	5.21	58.35	−25.71	6.40
8	0.065	,,	,,	5.24	62.61	−23.25	6.83
9	0.070	,,	,,	5.25	64.06	−16.10	6.17
10	0.075	,,	,,	5.29	70.13	−17.83	7.42
11	0.080	,,	,,	5.31	73.47	−14.88	7.58
12	0.099	,,	25.3°	5.40	90.44	−11.77	10.31
13	0.108	,,	,,	5.42	94.74	− 6.31	10.16
14	0.117	,,	28.8°	5.46	103.80	− 5.70	12.10
15	0.126	,,	25.3°	5.47	106.20	− 0.17	11.31
16	0.135	,,	,,	5.49	111.10	+ 3.12	11.65
17	0.050	0.010	33.0°	5.49	55.55	−25.07	5.87
18	0.100	,,	,,	5.72	94.24	− 4.17	9.66
19	0.200	,,	,,	5.93	152.54	+24.06	15.92
20	0.250	,,	,,	5.99	174.75	+36.16	17.89
21	0.050	0.050	28.5°	4.497	28.30	−36.77	2.88
22	,,	0.045	,,	4.587	31.30	−34.73	3.15
23	,,	0.040	,,	4.682	34.61	−33.56	3.52
24	,,	0.035	,,	4.786	38.49	−34.14	4.11
25	,,	0.030	,,	4.885	41.45	−31.12	4.30
26	,,	0.025	,,	4.991	44.07	−27.17	4.34
27	,,	0.020	,,	5.130	48.59	−28.78	5.16
28	,,	0.015	,,	5.270	50.28	−22.23	4.75
29	,,	0.010	,,	5.480	54.39	−21.99	5.35

* 'C' and 'C_a' denote respectively the molar conc. of $MnAc_2$ and HCl.

Experimental

Manganese acetate (Thomas Tyrer and Co., London) was purified by crystallising twice from acetic acid. The residue was then washed with ice-cold water and finally with ether. $Mn(CH_3COO)_2$, $4H_2O$ (Cadenhead and Vinning, *Can. Chem. Met.*, 1924, **8**, 64) requires Mn, 22.42% (found as sulphate : 22.50%).

Stock solutions of manganese acetate and hydrochloric acid were prepared. In these solutions manganese was estimated gravimetrically as sulphate and the strength of the acid solutions, by titration with a standard alkali. For preparation of solution mixtures, such volumes of manganese acetate and hydrochloric acid solutions were measured out that on dilution to 10 c.c., the desired initial concentrations 'C' and 'C_a' for manganese acetate and hydrochloric acid respectively were attained. After keeping the mixtures in a closed room for about three hours to reach equilibrium, the p_H values were determined by following the same procedure and observing the same precautions as described in Part II (*ibid.*, 1958, **35**, 279).

Table II

Soln. No. (as in Table I).	†$c_{MnAc^+} \times 10^3$.	†$c_{Mn^{++}} \times 10^3$.	$c_{MnAc_2} \times 10^3$. (Eq. 5).	μ (Part III, Eq. 10).	$c_{Ac^-} \times 10^3$ (Part III, Eq. 8b). $K_a = 1.75 \times 10^{-5}$.	$K_1 \times 10^1$ (Eq. 1a)	$K_2 \times 10^2$ (Eq. 2a).
1	6.94	16.84	1.22	0.05746	26.5	0.859 ‡	2.085
2	12.86	19.80	2.34	0.07226	43.3	1.266	1.886*
3	16.83	21.32	1.85	0.08079	53.6	2.500‡	1.785
4	18.53	21.89	4.58	0.08420	60.3	1.234	1.822
5	21.69	22.87	5.44	0.09030	65.7	1.293	1.688*
6	24.64	23.69	6.67	0.09571	72.7	1.298	1.633
7	28.87	24.74	6.39	0.10309	82.7	1.758	1.569*
8	31.80	25.40	7.80	0.10830	89.5	1.686	1.526
9	32.82	25.62	11.50	0.10968	91.9	1.199	1.514
10	37.15	26.49	11.36	0.11662	102.0	1.495	1.461*
11	39.59	26.94	13.47	0.12041	107.4	1.397	1.432
12	52.45	28.99	17.56	0.13942	136.2	1.690	1.303*
13	55.82	29.46	22.72	0.14420	144.0	1.449	1.276
14	63.05	30.37	23.58	0.15416	159.8	1.698	1.216
15	64.89	30.55	30.56	0.15669	164.3	1.377	1.204
16	68.91	31.04	35.05	0.16208	173.3	1.322	1.176*
17	23.40	21.07	5.53	0.08661	76.41	1.620	1.726
18	50.57	26.83	22.60	0.13106	140.00	1.336	1.351*
19	98.17	32.18	69.65	0.19471	250.00	1.250	1.030*
20	117.50	33.62	98.88	0.21836	291.66	1.157	0.929*
21	17.27	30.51	2.22	0.10880	40.5	1.452	1.519*
22	18.19	29.05	2.76	0.10534	44.6	1.371	1.550
23	19.18	27.71	3.11	0.10231	49.0	1.425	1.575
24	20.42	26.53	3.65	0.10001	54.3	1.729	1.597
25	20.94	25.25	3.81	0.09669	58.1	1.538	1.626*
26	21.13	23.97	4.90	0.09304	61.4	1.293	1.661
27	22.43	23.08	4.49	0.09167	67.4	1.654	1.672
28	21.84	21.72	6.44	0.08700	69.1	1.172	1.718
29	22.68	20.85	6.47	0.08523	74.5	1.316	1.737*

† Solving equations (4) and (9a) of Part III (*loc.cit.*) with a_{Ac^-} from Table I, these are calculated.

* These values have only been plotted on $pK/\sqrt{\mu}$ curve in Fig. 2 of Part VI (*loc.cit.*) where the points have been shown by □ mark. The values of 'K_2' without asteriks, if similarly plotted, will also fall on the same straight line, but this has not been done to avoid clumsiness in the figure.

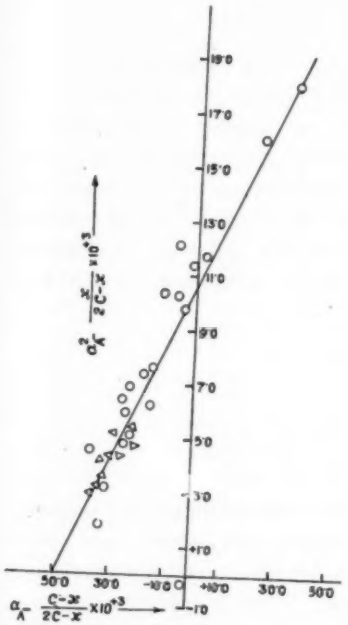
‡ These values were not considered while taking mean (vide : theoretical)

Table I shows the experimental p_H values and the corresponding values of the functions:

$$a_{A^-}{}^{2} \cdot \frac{C-x}{2C-x} \times 10^3 \text{ and } a_{A^-}{}^{2} \cdot \frac{x}{2C-x} \times 10^3$$

where A^- represents acetate ion and 'x', total concentration of "free acetic acid species" given by $c_{A^-} + C_a$). Fig. 1 represents equation (5b) (vide Part III, *loc. cit.*) graphically (using "$c_{A^-} = a_{A^-}$" in 5b for solutions of low ionic strengths). The slope and intercept on the ordinate of this straight line curve give the values of k_1 and k_2 as $k_1 = 210.0 \times 10^{-3}$ and $k_2 = 50.0 \times 10^{-3}$. These may be regarded as the average values of 'k_1' and 'k_2' over the range of ionic strengths employed. In Fig. 1 the circles represent data from Table I for the first 20 solution mixtures (Nos. 1 to 20) in which 'C_a' is constant and 'C' varying, and the triangles represent those for the last 9 solution mixtures (Nos. 20 to 29) in which 'C' is constant and 'C_a' varies. Table II, in which the values of 'K_1' and 'K_2' calculated by following the procedure already described, is self-explanatory.

FIG. 1



(Ordinate magnified 10 times of the abscissa).

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SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART VIII. NICKEL MONO-ACETATO COMPLEX

BY S. K. SIDDHANTA AND S. N. BANERJEE

The composition of the complex formed between Ni^{2+} and acetate ions has been found to be $NiAc^+$, from a study of the equilibrium H^+-concentrations in mixtures of equimolecular nickel nitrate and acetic acid solutions, with the help of "Job's method of continued variation", employing the increase of H^+-concentration as a new index property.

The thermodynamic dissociation constant, K, for the equilibrium $NiAc^+ \rightleftharpoons Ni^{2+} + Ac^-$ has been found out as 75.9×10^{-3} at 21.3–22.0°, as in Part I of this series.

The same procedure as adopted in Part I (this *Journal*, 1958, **35**, 269) was followed to determine the thermodynamic dissociation constant for the equilibrium,

$$NiAc^+ \rightleftharpoons Ni^{2+} + Ac^-$$

(where Ac^- represents acetate ion)

$$K = \frac{a_{Ni^{2+}} \cdot a_{Ac^-}}{a_{NiAc^+}} = \frac{c_{Ni^{2+}} \cdot c_{Ac^-}}{c_{NiAc^+}} \cdot \frac{f_{Ni^{2+}} \cdot f_{Ac^-}}{f_{NiAc^+}}, \qquad \ldots (1)$$

from a study of the p_H of solution mixtures containing '$1-x$' volume of nickel nitrate and 'x' volume of acetic acid, 'x' varying from 0.1 to 0.9, and both parent solutions being at the same concentration, 'C'. The composition of the complex formed has been determined, as in the case of lead acetate (Part I, *loc. cit.*). From $Y-x$ plots it has been observed that the maximum value of 'Y' corresponds to the reacting proportion 1 : 1 for nickel nitrate and acetic acid. It is evident therefore that under the condition of the experiment, the following equilibrium alone is most predominant, and the formation of higher complexes, e.g., $NiAc_2$, $NiAc_3$ etc., is negligible. The reaction thus becomes

$$Ni^{2+} + HAc \rightleftharpoons NiAc^+ + H^+.$$

Experimental

Nickel nitrate and acetic acid were of A.R. quality. All solutions were prepared with conductivity water. Stock solutions of nickel nitrate and acetic acid were prepared, and in these solutions nickel was determined with dimethylglyoxime and acetic acid, by titration with a standard alkali solution. After keeping the mixtures in a closed room for 4 hours, the p_H values were determined by following the same procedure and observing the same precautions as were done in Part II (*ibid.*, 58, **35**, 279).

Fig. 1

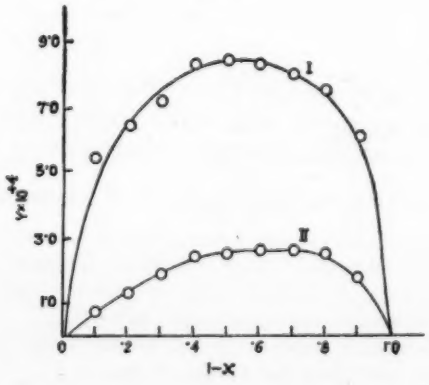


TABLE I

(HAc represents acetic acid)

$1-x$.	Solution mixtures in c.c.			Concentration of parent solutions. $M/5$; $C=0.2$; $p=1$; temp. $=21.3°$.		$M/10$; $C=0.1$; $p=1$; temp. $=22°$.	
	HAc.	$Ni(NO_3)_2$.	H_2O.	p_H.	Increase in $[H^+]$, $(Y\times10^4)$.	p_H.	Increase in $[H^+]$, $(Y\times10^4)$.
	9	1	...	2.690	5.42	2.882	0.70
0.1	9	...	1	2.824		*(12.42)	
	8	2	...	2.673	6.44	2.882	1.36
0.2	8	...	2	2.830		(11.76)	
	7	3	...	2.673	7.17	2.887	1.91
0.3	7	...	3	2.852		(11.06)	
	6	4	...	2.673	8.32	2.897	2.54
0.4	6	...	4	2.889		(10.14)	
	5	5	...	2.690	8.40	2.928	2.55
0.5	5	...	5	2.920		(9.25)	
	4	6	...	2.724	8.32	2.964	2.62
0.6	4	...	6	2.980		(8.24)	
	3	7	...	2.767	7.98	3.007	2.66
0.7	3	...	7	3.040		(7.18)	
	2	8	...	2.830	7.51	3.079	2.54
0.8	2	...	8	3.138		(5.80)	
	1	9	...	2.957	6.11	3.226	1.84
0.9	1	...	9	3.307		(4.10)	

N. B. In the present case the hydrogen-ion concentration of the mixture of '$1-x$' c.c. of nickel nitrate solution at concentrations $C=0.2$ and $C=0.1$ with 'x' c c. of water is very small and has therefore been neglected in calculating the value of 'Y'.

* In this case with $C=0.1$, the $[H^+]$ ($\approx a_H{}^+\times10^4$) for the acetic acid solutions are calculated from the relations,

$$K_a = \frac{C\alpha^2}{1-\alpha} \quad \text{and} \quad [H^+]=\alpha C,$$

where α is the degree of dissociation of acetic acid; C is the concentration of acetic acid and K_a, the ionisation constant of acetic acid at 22° (1.75×10^{-5} from "Physical Chemistry of Electrolytic Solutions" by Harned and Owen, 2nd. ed., p. 580). These values are shown in parentheses.

TABLE II

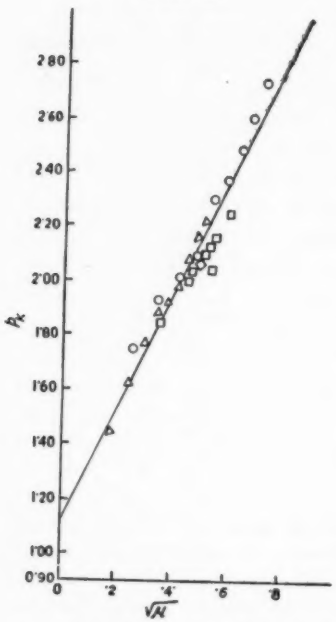
The symbols used in the table headings and their evaluations are same as in Part I (*loc. cit.*).

$1-x$.	Solution mixtures in c.c.		Concentration of parent solutions. $M/5$; $C=0.2$; $p=1$; temp. $=21.3°$.		$M/10$; $C=0.1$; $p=1$; temp. $=22°$.	
	HAc.	$Ni(NO_3)_2$.	μ.	$K\times10^5$.	μ.	$K\times10^5$.
0.1	9	1	0.0610	17.56	0.0310	35.76
0.2	8	2	0.1205	11.80	0.0607	23.69
0.3	7	3	0.1801	8.96	0.0903	16.83
0.4	6	4	0.2398	6.42	0.1203	13.11
0.5	5	5	0.2996	5.05	0.1503	12.07
0.6	4	6	0.3596	4.27	0.1802	10.47
0.7	3	7	0.4195	3.33	0.2100	8.37
0.8	2	8	0.4794	2.53	0.2399	6.91
0.9	1	9	0.5395	1.87	0.2699	6.09

N. B. Taken ionisation constant of acetic acid to be 1.75×10^{-5} (Harned and Owen, *loc. cit.*).

The results of p_H determinations for mixtures of two sets of equimolar parent solutions of nickel nitrate and acetic acid, one having concentration $C=0.2$ and another set $C=0.1$, have been shown in Table I. The values of 'Y' against the corresponding values of 'x' from Table I, for mixtures of nickel nitrate and acetic acid solutions, both being at concentration $C=0.2M$, have been graphically represented by curve I, and those for both parent salutions at concentration $C=0.1M$, by curve II, in Fig. 1. The values of 'μ' and 'K' for the solution mixtures, studied in the present work, have been obtained by following the same procedure as described in Part I (*loc. cit.*) and these are shown in Table II. As in the previous case (vide Part I), the plot of 'K' against 'μ' from Table II yields a smooth curve, which has not been used to evaluate the value of 'K' by extrapolation to zero ionic strength. In Fig. 2, the graph pK $(=-\log K)$ against $\sqrt{\mu}$ from Table II gives a straight line curve which on extrapolation to $\sqrt{\mu}=0$ gives the value of pK corresponding to the true thermodynamic constant, K. These values of 'pK' and 'K' at $\sqrt{\mu}=0$ are 1.12 and 75.9×10^{-3} at 21.3-22° respectively.

FIG. 2



(The sign □ represents the plot of pK_2/μ from Table II of part IX).

Critical comments on the previous work on the subject, as also on the present work have been made in Part IX of this series.

The authors' best thanks are due to Prof. S. K. Bhattacharyya for offering all the facilities to do this work.

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SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART IX. NICKEL ACETATO COMPLEXES

BY S. K. SIDDHANTA AND S. N. BANERJEE

p_H values of aqueous solution mixtures of nickel acetate and nitric acid at different concentrations, after attainment of equilibrium, have been determined and the data obtained have been utilised to calculate the mass action constants, K_1 and K_2, for the two successive equilibria, $NiAc_2 \rightleftharpoons NiAc^+ + Ac^-$ and $NiAc^- \rightleftharpoons Ni^{2+} + Ac^-$, by applying Bjerrum's method. The inapplicability of the method of Siddhanta and Banerjee (Part III) has been accounted for and a method has been suggested to calculate the values of thermodynamic dissociation constants, K_1 and K_2, in a similar way as described in Part VII of the series.

Nickel acetate dissociates in aqueous solution in two stages:

$$NiAc_2 \rightleftharpoons NiAc^+ + Ac^- \quad \ldots \quad \ldots \quad (A)$$

$$NiAc^+ \rightleftharpoons Ni^{2+} + Ac^- \quad \ldots \quad (B)$$

In this paper the thermodynamic dissociation constants, 'K_1' and 'K_2' (equations 1 and 2) have been determined from a measurement of p_H of solution mixtures of nickel acetate and nitric acid by adopting exactly the same procedure as followed in the case of manganese acetate (Part VII, *issue*, p. 419).

$$K_1 = \frac{c_{NiAc^+} \cdot c_{Ac^-}}{c_{NiAc_2}} \cdot \frac{f_{NiAc^+} \cdot f_{Ac^-}}{f_{NiAc_2}} \quad \ldots \quad \ldots \quad (1)$$

and

$$K_2 = \frac{c_{Ni^{2+}} \cdot c_{Ac^-}}{c_{NiAc^+}} \cdot \frac{f_{Ni^{2+}} \cdot f_{Ac^-}}{f_{NiAc^+}} \quad \ldots \quad \ldots \quad (2)$$

The procedure employed in the case of lead acetate (Part III, this *Journal*, 1958, **35**, 323) could not be adopted here for exactly the same reasons as described in the case of manganese acetate (Part VII, *loc. cit.*). By averaging all the values of 'K_1' obtained in Table II, we get $K_1 = 2.06 \times 10^{-1}$ at room temperature. As in the case of manganese acetate (Part VII, *loc. cit.*), the value of 'K_1', obtained here, is not at all accurate and is only indicative of the order. The value of 'K_2', however, is fairly accurate, as it has been found out by graphical extrapolation to $\sqrt{\mu} = 0$. The $pK_2/\sqrt{\mu}$ plot from the data in this paper has been shown by □ mark in the $pK/\sqrt{\mu}$ plot for nickel nitrate and acetic acid mixtures, represented in Fig. 2 in Part VIII (this *issue*, p. 423). It will be seen that all these points fall on the same straight line as that representing $pK/\sqrt{\mu}$ obtained from the data for nickel nitrate and acetic acid mixtures (Part VIII, *loc. cit.*). The value of the thermodynamic constant 'K_2' is therefore same as that obtained in Part VIII, and it is $K_2 = 75.9 \times 10^{-3}$ at room temperature.

Experimental

Nickel acetate (Fine chemical, Hopkins, and Williams Ltd., London) was purified by crystallising from acetic acid. The residue was then washed with ice-cold water and finally with ether. [Calc. for $Ni(CH_3COO)_2$, $4H_2O$: Ni, 23.60%. Found: Ni, 23.40%).

Stock solutions of nickel acetate and nitric acid were prepared in which nickel was estimated with dimethylglyoxime and the strength of the acid by standard alkali titration. In the preparation of solution mixtures such calculated volumes of stock solutions were taken from a microburette that on diluting the mixture to 10 c.c., the desired initial concentrations, C and C_a, for nickel acetate and nitric acid respectively, were obtained. After keeping the mixtures in a closed room for about 4 hours to reach equilibrium, the p_H values were determined by following the same procedure and observing the same precautions as described in Part II (*ibid*, 1958, **35**, 279) of this work.

TABLE I

The symbols used in the table headings and their evaluations are same as in Part III (*loc. cit.*) of this work.

Soln. No.	C.*	C_a.*	$t°$.	p_H.	$a_A \times 10^3$ ($K_a = 1.80 \times 10^{-5}$).	$a_A - \frac{C-x}{2C-x} \times 10^3$.	$a_A - 2\frac{x}{2C-x} \times 10^3$.
1	0.045	0.050	32.8	4.398	22.51	−35.40	2.10
2	0.060	,,	32.5	4.646	39.85	−39.42	4.73
3	0.075	,,	32.8	4.764	52.26	−29.84	5.85
4	0.090	,,	32.5	4.882	68.60	−31.95	9.09
5	0.105	,,	32.8	4.940	78.40	−22.47	9.66
6	0.120	,,	32.5	5.003	90.60	−18.77	11.61
7	0.135	,,	32.8	5.05	101.01	−13.59	12.94
8	0.150	,,	32.5	5.09	110.70	− 8.50	14.13
9	0.165	,,	32.8	5.12	118.58	− 2.62	14.63
10	0.180	,,	32.5	5.17	133.10	− 2.33	18.33
11	0.195	,,	32.8	5.20	142.63	+ 1.71	19.85
12	0.210	,,	32.5	5.23	152.80	+ 5.06	21.80
13	0.225	,,	32.8	5.23	152.80	+13.72	19.15
14	0.240	,,	32.5	5.27	167.55	+14.33	23.27
15	0.300	,,	33.5	5.35	201.30	+28.11	29.20
16	0.360	,,	,,	5.40	226.10	+42.73	31.79
17	0.420	,,	,,	5.44	247.90	+55.83	33.77
18	0.480	,,	,,	5.49	277.75	+66.88	39.99
19	0.180	0.036	33.0	5.40	135.67	+10.01	15.68
20	,,	0.045	,,	5.20	128.34	+ 4.57	15.29
21	,,	0.060	,,	5.03	115.74	+ 2.67	12.77
22	,,	0.075	,,	4.921	112.58	− 4.94	13 78
23	,,	0.090	,,	4.817	106.29	−10.57	13.54
24	,,	0.100	32.3	4.762	104.04	−16.03	14.16
25	,,	0.105	33.0	4.727	100.80	−16.86	13.56
26	,,	0.1125	32.3	4.691	99.41	−21.42	14.14
27	,,	0.125	,,	4.599	89.35	−21.07	11.74
28	,,	0.1375	,,	4.539	85.61	−26.96	11.94
29	,,	0.150	,,	4.468	79.50	−30.15	11.11
30	,,	0.1625	,,	4.386	71.14	−30.19	9.30
31	,,	0.175	,,	4 325	66.55	−34 58	9.03

* C and C_a denote respectively the molar conc. of $NiAc_2$ and HNO_3.

TABLE II

Soln. No. (as per Table I).	$^{**}c_{NiAc^+} \times 10^3$.	$^{**}c_{Ni^{2+}} \times 10^3$.	$c_{NiAc_2} \times 10^3$ (Part. VII, Eq. 5).	μ (Part III, Eq. 10).	$c_{Ac^-} \times 10^3$ (Pt. III, Eq. 8b) $K_a = 1.75 \times 10^{-5}$.	$K_1 \times 10^{+1}$ (Eq. 1).	$K_2' \times 10^2$ (Eq. 2).
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	13.32	29.59	2.09	0.10209	31.82	0.957‡	1.575
2	25.60	32.12	2.28	0.12196	58.40	2.887	1.420*
3	35.09	33 58	6.33	0.13583	78.33	1.828	1.327
4	48.25	35.17	6.58	0.15376	105.67	3.085‡	1.220
5	56.42	35.99	12.56	0.16439	122.7	2.122	1.165
6	66.83	36 88	16.29	0.17747	144.6	2.204	1.101
7	75.88	37.56	21.56	0.18856	163.55	2.076	1.052
8	84.42	38.14	27.44	0.19884	181.53	1.960	1.009
9	91.45	38.56	34.99	0.20713	196.6	1.765	0.977
10	104.55	39.27	36.18	0.22236	224.9	2.147	0.922*
11	113.23	39.70	42.07	0.23233	244.41	2.121	0.891
12	122.57	40.12	47.31	0.24292	265.15	2.159	0.856
13	122.57	40.11	62.32	0.24290	265.2	1.640	0.858*
14	136.23	40.66	63.11	0 25821	295.6	1.935	0.812
15	167.89	40.70	90 41	0.29299	369.2	1.922	0.721*
16	191.43	42.33	126.24	0.31842	426.8	1.720	0.666
17	212.27	42.81	164.92	0.34070	478.14	1.563	0.621
18	240.98	43.38	195.64	0.37112	553.8	1.631	0.570*
19	95.37	35.15	49.48	0.20082	223.4	1.503	1.003*
20	97.42	37.96	44.62	0.21130	213.99	1.587	0.962
21	94.28	40.73	44.99	0.21647	194.4	1.365	0.943
22	99.34	44.12	36 54	0.23170	192.73	1.692	0.891
23	101.13	47.58	31.29	0.24387	184.6	1.870	0.853
24	104.03	50.00	25.97	0.25403	182.86	2.243	0.823
25	103 31	51.24	25.45	0.25703	177.7	2.192	0.814
26	105.64	53.13	21.23	0.26503	176.89	2.627	0.792*
27	101.14	56.60	22 26	0.27094	160 1	2.141	0.776
28	102.90	60.10	17.00	0.28320	155.44	2.696	0.745*
29	101.64	63.93	14.43	0.29343	145 9	2.879	0.720
30	97.12	68.26	14.62	0.30190	131.84	2.410	0.701*
31	96.51	72.52	10.97	0.31407	125.0	2.947	0.675

* Solving equations (4) and (9a) of Part III (*loc. cit.*) with a_{Ac^-} from Table I, these are calculated.

* These values have been plotted on pK 1 $\sqrt{\mu}$ curve in Fig. 2 of Part VIII (*loc. cit.*) of this work, where the points have been shown by □ mark. The values of 'K_2' without asteriks, if similarly plotted, will also fall on the same straight line, but this has not been done to avoid clumsiness in the figure.

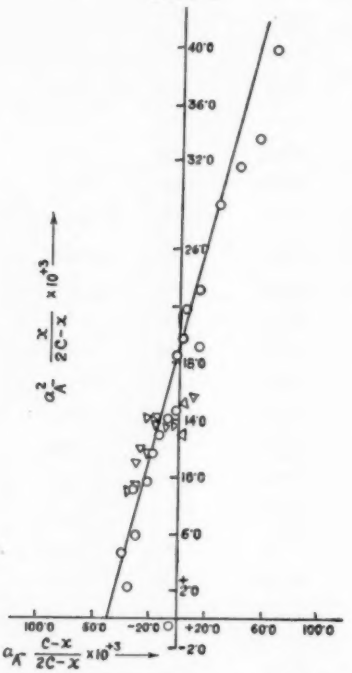
‡ These values were not considered while taking mean (vide : theoretical).

Table I shows the experimental p_H values and the corresponding values for the function :

$$a_{A^-}\cdot\frac{C-x}{2C-x}\times 10^3 \text{ and } a_{A^-}{}^2\cdot\frac{x}{2C-x}\times 10^3$$

(where A^- represents acetate ion and 'x', total concentration of "free acetic acid species" given by $c_{A^-} + C_a$). Fig. 1 represents equation (5b) (vide Part III, *loc. cit.*) graphically (c_{A^-} may be put equal to a_{A^-} in eq. 5b for solution of low ionic strengths). The slope and intercept on the ordinate of this straight line curve give the values of k_1 and k_2, as 384×10^{-3} and 50×10^{-3} respectively. These are the average values of 'k_1' and 'k_2' over the range of ionic strengths employed. In Fig. 1 the circles represent the data from Table I for the first 18 solutions (No. 1 to 18) where 'C_a' is constant and 'C' varying, and the triangles represent those for the last 13 solutions (No. 19 to 31) in which 'C' is constant and 'C_a' varying. Table II, in which the values of 'K_1' and 'K_2' have been calculated by following the procedure already described, is self-explanatory.

FIG. 1



(Ordinate magnified 10 times of the abs.)

DISCUSSION

The only previous work on the subject appears to be that of Jana, Aditya and Prasad (this *Journal*, 1953, **30**, 735) who from the E. M. F. measurements of the cells of the type,

$$\underset{}{\text{Hg, } Hg_2Ac_2 \mid \underset{c}{BaAc_2}, \underset{c_1}{HAc} \parallel \underset{KCl\ bridge}{\text{Half salt}} \parallel \underset{c}{NiAc_2}, \underset{c_2}{HAc} \mid Hg_2Ac_2, \text{ Hg}}$$

conclude that the first stage dissociation of nickel acetate in aqueous solution is virtually complete, and the thermodynamic constant for the equilibrium (B) representing the second stage dissociation is given by $K_2 = 7.41\times10^{-2}$ at 30-32 5°. The method of calculation used by the authors in the above paper is open to the objection that the effect of the presence of acetic acid in the nickel acetate solution has not been taken into account in the calculation of the dissociation 'β' for $NiAc^+$. Moreover, the authors by making an *ad hoc* assumption, that the first stage dissociation is complete, compute a value of 'K_2' and then using this value of 'K_2' they try to arrive at a value of 'α', the degree of dissociation for $NiAc_2$ into $NiAc^+$ and Ac^-. Since they find that 'α', thus obtained, is nearly 1, they conclude that the first step

dissociation is complete. This method is theoretically less sound than the present one which takes into account the effect of both dissociations simultaneously. However, from the magnitude of 'K_1' obtained in this paper and from the values of c_{NiAc}, (vide Table II), the present authors have no hesitation to assert that the first stage dissociation proceeds to a much larger extent than in the cases of other acetates studied in this series.

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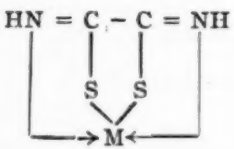
RUBEANIC ACID AND ITS DERIVATIVES AS COLORIMETRIC REAGENTS. PART I. SPECTROPHOTOMETRIC DETERMINATION OF COBALT, NICKEL, PALLADIUM, SILVER AND RUTHENIUM WITH RUBEANIC ACID

By J. Xavier and Privadaranjan Rây

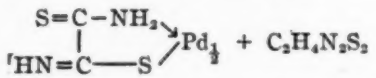
Methods for the spectrophotometric determination of cobalt, nickel and palladium in alcoholic pyridine solutions with rubeanic acid are described. Cobalt has been estimated in presence of copper, nickel and silver by employing potassium cyanide and thiourea as masking agents. An extraction procedure for palladium with *iso*amyl alcohol, using disodium salt of ethylenediamine tetra-acetic acid as sequestering agent, is also described. A method of estimating silver in aqueous medium at p_H 4.0–4.6 has been developed. The method for determining ruthenium, as reported by Ayres and Young (*Anal. Chem.*, 1950, **22**, 1281), has been modified and improved. The colour system in all cases more or less obeys Beer's law and gives values of high sensitivity.

Rubeanic acid has been extensively used as a sensitive and selective colorimetric reagent since its introduction by Ray and Rây (this *Journal*, 1926, **3**, 118). It reacts with solutions of Cu^{II}, Co^{II}, Ni^{II}, Pd^{II}, Au^{III}, Pt^{II}, Ag^{I}, Hg^{II}, Cd^{II}, Fe^{II} and Tl^{I}, forming coloured precipitates. These precipitates, with the exception of those of iron, gold, mercury, lead, cadmium and thallium, are quite stable at the room temperature.

The acidic character of the reagent depends on its tautomerism among the diamido (baso), the amidoimido (semiaci) and the diimido (aci) forms, the latter two containing the aci group, —SH. The complex compounds of rubeanic acid with bivalent metals have been accordingly assigned an inner metallic structure :



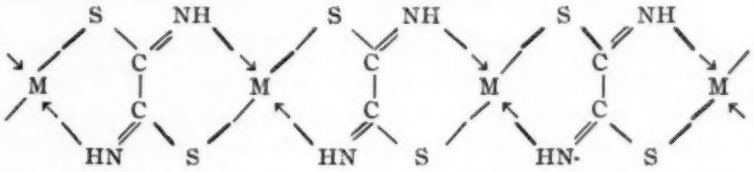
Wolbling and Steiger (*Mikrochem.*, 1934, **15**, 295), on the basis of analytical results, suggested the following formula for its palladium salt :



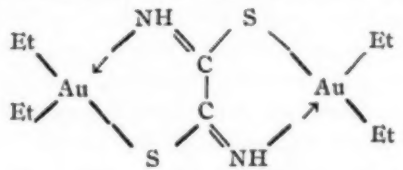
However, the possibility of a palladium salt of the aci-form, co-ordinated with two molecules of rubeanic acid, has been indicated by Feigl ("Chemistry of Specific, Selective and Sensitive Reactions", Academic Press Inc., Publishers, New York, p. 250, 1949). Bobtelsky and Eisenstadter (*Anal. Chim. Acta*, 1957, **17**, 579) also have reported the formation of compounds like Pd_3R_2, Pd_1R_1, Pd_2R_3 and Pd_1R_2 (where R=1 mol. of rubeanic acid), depending on the concentration of the reagent

and p_H of the medium. Spectrophotometric data indicate that Ru^{III} and Ru^{IV} form the same complexes, $[Ru\ SC(NH)CSNH_2]^{2+}$ and $[Ru\ \{SC(NH)CSNH_2\}_3]$ (Yaffe and Voigt, *J. Amer. Chem. Soc.*, 1952, **74**, 3163).

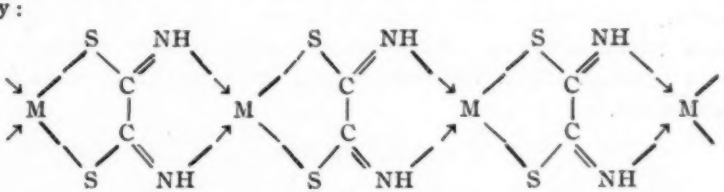
In analogy with certain nickel mercaptides, Jensen (*Z. anorg. Chem*, 1944, **252**, 227) considers that the nickel salt of rubeanic acid cannot be a monomeric complex, but it must be formulated with a polymeric structure:



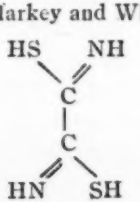
In this, the functioning groups of the ligand are arranged in a *trans* configuration around the central metal ion. This assumption has been strengthened by the work of Amon and Kane (U. S. P., 2, 505, 085/1950; cf. also Bailaf Jr., "The Chemistry of Co-ordination Compounds", p. 56, Reinhold Publishing Corpn., New York, 1956) who found that when a plastic sheet covered with the precipitate of rubeanic acid metal complex was stretched in one direction, the polymer chains were oriented parallel to each other, which alone could account for the polarisation of transmitted light. The bridging ability of rubeanic acid might also be inferred from a consideration of the structure of the diethyl gold derivative of dithiooxamide (Ewens and Gibson, *J. Chem. Soc.*, 1949, 431).



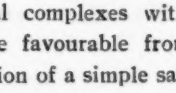
A polymeric structure with a *cis* configuration of the following type is also not unlikely:



though the crystal structure of rubeanic acid, as revealed by X-ray measurement is given by a *trans*-form (Long, Markey and Wheatley, *Acta Cryst.*, 1954. **7**, 140):



But in solution, the rotation of the compound along the C—C axis might be possible, leading to the formation of metal complexes with a *cis* configuration. The *trans*-form, however, seems to be more favourable from symmetry and steric consideration. The possibility of the formation of a simple salt of the type,



is not likely, as the magnetic values of the nickel and cobalt rubeanates differ widely from those of their simple salts (Rây and Bhar, this *Journal*, 1928, **5**, 499).

Certain solvents, in which most of the precipitated metal complexes of rubeanic acid and of its derivatives are only sparingly soluble, can, however, extract the latter from their solutions in pyridine. For example, the cobalt, nickel and palladium rubeanates are easily extracted from their pyridine solution by *iso*butyl or *iso*amyl alcohol, in which the precipitated metal complexes are very sparingly soluble. This seems to suggest that the precipitated polymerised complex rubeanates dissolve in pyridine, possibly giving rise to a pyridine complex of the monomer.

Spot tests and capillary separation methods were employed in the detection of copper, cobalt, nickel, etc. by Rây and other workers (Welcher, "Organic Analytical Reagents", Vol. IV, p. 148, V. Nostrand Comp., Inc., New York, 1948). Methods of estimating copper spectrophotometrically, as described by various workers (Welcher, *loc. cit.*; West and Compere, *Anal. Chem.*, 1949, **21**, 628; Miller *et al.*, *Metal Abst.*, 1952, **19**, 856; Steinle and Lollar, *J. Amer. Leather Chem. Assoc.*, 1954, **49**, 285), involve a great difficulty due to extreme insolubility of the copper compound in aqueous solution. Hence, protective colloids, such as gelatine and gum arabic, have been used for peptisation.

The solubility of nickel rubeanate in pyridine (Ray and Rây, *loc. cit.*) suggested the possibility of a colorimetric estimation of the metal. In fact, pyridine is found to be the most suitable solvent for cobalt, nickel and palladium rubeanates. Solutions in acetone or triethanolamine are less stable. Benzene, toluene, carbon tetrachloride, chloroform, ethyl or amyl acetate, *iso*amyl or *iso*butyl alcohol, etc. have little solvent action on the metal rubeanates. Copper rubeanate is sparingly soluble in pyridine. Silver rubeanate is sufficiently soluble in water for its colorimetric estimation.

EXPERIMENTAL

Determination of Cobalt

Cobalt was determined in alcoholic pyridine solution with rubeanic acid, by measuring the colour intensity at 400 mμ, at p_H 6.5–7.2. The colour remained unchanged for about 2 hours, and the system was found to obey Beer's law. The sensitivity of the reaction is 0.0043γ Co/cm^2 (Sandell) and 0.01γ Co/cm^2 (practical). Interferences due to small amounts of nickel, copper and silver may be eliminated by the addition of potassium cyanide and thiourea solutions respectively.

The optical density measurements in the visible region were made with a Unicam SP 600 spectrophotometer, using glass cells having 0.5 cm, 1 cm or 2 cm cross-sections. All p_H measurements or adjustments were made with the help of a Cambridge Bench Type p_H-meter, using glass or alkali electrode and a calomel reference electrode.

Standard cobalt solution was prepared by dissolving cobalt chloride (E. Merck, G.R. quality) in distilled water. The cobalt content of this solution was determined as $CoSO_4$.

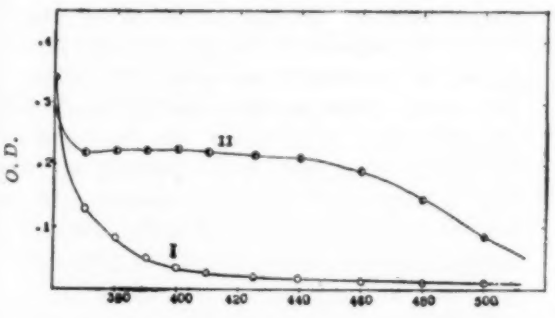
A 0.1% (w/v) solution of rubeanic acid (prepared by the method of Wollner, *J. prakt. Chem.*, 1884, **29**, 129) in 95% ethyl alcohol was prepared. This solution remains generally stable for several days.

Freshly distilled pyridine was used for all estimations. L.R. (B.D.H.) quality of pyridine was twice distilled in an all-glass apparatus, and the portion distilling at 115-16° was collected.

A 1% potassium cyanide (E. Merck, Extra Pure quality) solution in water was prepared. An almost saturated aqueous solution of thiourea (7-8 g. in 100 c.c. at 25°) was used.

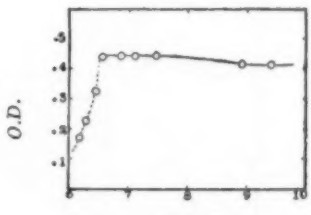
Absorption Curves.—The orange-yellow coloured solution of the complex shows maximum absorption in the ultraviolet region. But rubeanic acid also shows a rather high absorption in that region. Measurements were therefore made at 400 mμ, where the absorption of the reagent was comparatively small. Fig. 1 shows the absorption curves of blank (I) and of test solution (II). The absorption of the complex solution against reagent blank is almost constant between 380 and 400 mμ.

FIG. 1



Co=0.974 p.p.m. p_H = 6.8. Cell = 1cm.

FIG. 2



Co=1.96 p.p.m.

Concentration of Pyridine and Alcohol.—Pyridine (2-3 c.c.), added to the metal salt solution previous to the addition of the reagent, was sufficient to keep the complex in alcoholic (over 70%) solution (25 c.c. final volume).

Reagent Concentration.—A 0.1 % solution (1 c.c.) of rubeanic acid was sufficient for an amount of cobalt up to 0.1 mg. Addition of an excess of the reagent had no effect on the optical density of the solution.

Effect of p_H was studied with cobalt solutions containing 1.96 γ Co/c.c. and 3 c.c. of pyridine in a final volume of 25 c.c. Optinum p_H = 6.5-7.2 (cf. Fig. 2). The optical density of the blank solution was unaffected by p_H changes.

Beer's Law.—Fig. 3-A shows that the system adheres to Beer's law.

Stability of the Colour.—A solution containing 2γ Co/c.c., pyridine (2 c.c.) and 1 c.c. of rubeanic acid (total volume 25 c.c.) at p_H 6.8–7.0 showed the same absorption for 4 hours. With higher concentrations of cobalt (4γ), opalescence appeared after 2 hours. The colour was found to be stable below 35°.

Sensitivity.—0.0043 γ Co/cm² (Sandell) and 0.01 γ Co/per cm² (practical).

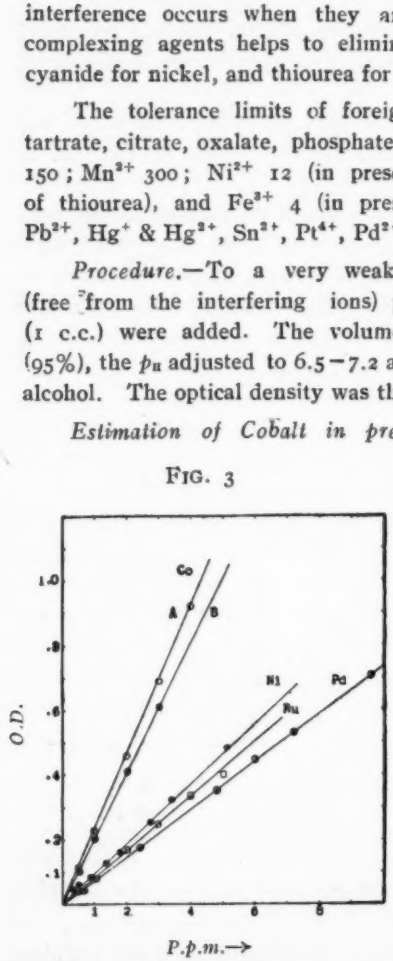
Effect of Diverse Ions.—Since rubeanic acid reacts with a number of metals, interference occurs when they are present even in small amounts. Addition of complexing agents helps to eliminate this interefrence in certain cases, e.g., potassium cyanide for nickel, and thiourea for copper and silver.

The tolerance limits of foreign ions (p.p.m.) for 2 p.p.m. Co are: acetate 100, tartrate, citrate, oxalate, phosphate and fluoride 50; MoO_4^{2-} and WO_4^{2-} 500; VO_3^- 150; Mn^{2+} 300; Ni^{2+} 12 (in presence of KCN), Ag^+ 20 and Cu^{2+} 8 (in presence of thiourea), and Fe^{3+} 4 (in presence of fluoride). Bi^{3+}, Cr^{3+}, Fe^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Hg^+ & Hg^{2+}, Sn^{2+}, Pt^{4+}, Pd^{2+} and Au^{3+} interfere even in very small amounts.

Procedure.—To a very weakly acidic or an almost neutral solution of cobalt (free from the interfering ions) pyridine (2-3 c.c.) and the reagent solution (1 c.c.) were added. The volume was made nearly to 20 c.c. with ethyl alcohol (95%), the p_H adjusted to 6.5–7.2 and the solution finally made up to 25 c.c. with alcohol. The optical density was then measured at 400 mμ against a reagent blank.

Estimation of Cobalt in presence of Nickel.—By the addition of potassium cyanide solution, the pink colour of the nickel complex is completely discharged, while the yellow colour due to cobalt is not appreciably affected. The colour system was found to obey Beer's law (cf. Fig. 3-B). The colour was developed as described above, and before making up the volume, 1 c.c. of 1% potassium cyanide solution was added, followed by 5 c.c. of water. Potassium cyanide solution should always be added only after the development of the colour at the desired p_H values and the optical density measured within half an hour, before the appearance of any precipitate.

FIG. 3



Estimation of Cobalt in presence of Copper and Silver.—To the cobalt solution containing copper and/or silver, thiourea solution (5 c.c.) was added, successively followed by 3 c.c. of water, 2 c.c. of pyridine, 1 c.c. of rubeanic acid solution (p_H now adjusted to 6.5–7.2) and 1 c.c. of KCN solution and the volume made up to 25 c.c. with alcohol. The optical

density was measured at 400 mμ against a suitable blank. The tolerance limit, when both copper and silver are present together with 2 p.p.m. cobalt, is 4 p.p.m. of each.

Estimation of Cobalt in presence of Iron.—Ferric iron develops a yellow colour or turbidity with pyridine, although it does not form any strongly coloured complex with rubeanic acid. Addition of sodium fluoride prevents this. 4 P.p.m. of iron (Fe^{3+}) for 2 p.p.m. of Co is tolerated with 1 c.c. of 0.5% solution of sodium fluoride added before the addition of pyridine and the reagent. The volume is made up as usual to 25 c.c. with alcohol and water (5 c.c.). However, the solution becomes opalescent within 10 to 15 minutes. Hence, measurements were immediately taken after the solution was made up. This method is quite suitable for the detection of cobalt even in the presence of a large amount of iron.

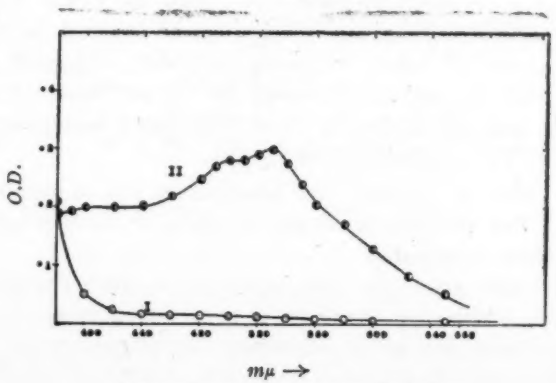
Determination of Nickel

The nickel rubeanate in pyridine yields a pink-coloured solution, which permits the determination of the metal when present in traces. The optical density of the solution, measured at 580 mμ (p_H 9.5-10.5), was found to obey Beer's law for concentrations of nickel above 1 p.p.m., and gave a sensitivity of 0.011 γ Ni/cm² (Sandell). The method, though highly sensitive, requires, as in the case of many other standard methods, a preliminary separation of nickel from metals like iron, cobalt, and also from copper, except when using thiourea.

Standard nickel solution was prepared by dissolving a known quantity of nickel chloride (E. Merck, G. R. quality) in distilled water, and determining the nickel content of the solution with dimethylglyoxime. Rubeanic acid, pyridine and thiourea solutions were the same as used in the estimation of cobalt.

Absorption Curves.—The pink coloured solution has an absorption maximum at 530 mμ, where the reagent solution shows negligible absorption. Fig. 4 shows the absorption curves of the reagent blank and of nickel rubeanate solutions. The optical density is almost constant between 400 and 440 mμ, but is maximum at 530 mμ where measurements were made.

FIG. 4



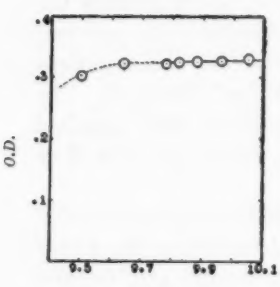
Ni=3.2 p.p.m. p_H = 10.1. Cell=1 cm.

Concentration of Pyridine and Alcohol.—The amount of pyridine added, with all other factors remaning constant (Ni 3 p.p.m., 1 c.c. reagent and $p_H \simeq 10$), was varied. The stability and the optical density of the colour system were found to increase with pyridine concentration. Solutions containing 5,10,15 and 20 c.c. pyridine in a total volume of 25 c.c. were stable for about 1, 1½, 2½ and 3 hours respectively. Hence, the addition of an excess of pyridine (15-20 c.c.) is necessary for the stability of the solution ; this, however, raises its p_H value. The final volume was made up with 95% ethyl alcohol, since water caused turbidity.

Reagent Concentration.—A 0.1% alcoholic rubeanic acid solution (1 c.c.) was sufficient to develop the maximum colour intensity with nickel concentration below 0.2 mg. The optical density was not altered by an excess of the reagent.

Effect of p_H.—The colour intensity was stable for about 2-3 hours at p_H 9.5–10.5. But a p_H above 9.8 was preferable at which the colour development was almost instantaneous. Below p_H 9.0, the colour tint was more or less yellow to begin with, which gradually changed to violet and became finally pink. Fig. 5 shows the effect of p_H on the optical density of a solution containing 3.4γNi/c.c., 15 c.c. of pyridine and 1 c.c. of rubeanic acid solution in a total volume of 25 c.c. The measurements were made against water as blank, as the reagent solution was kept constant and was unaffected by p_H change.

FIG. 5



Ni=3.4 p.p.m.

Beer's Law.—The system was found to obey Beer's law with nickel concentration exceeding 1 p.p.m. (cf. Fig. 3).

Stability of the Colour.—The absorption of a solution (p_H 10.2) containing 3.4 p.p.m. of Ni, 1 c.c. of rubeanic acid solution and 15 c.c. of pyridine showed no change in optical density for about 3 hours, after which opalescence occurred. The colour was also stable at temperatures up to 35°.

Sensitivity.—0.011γNi/cm² (Sandell) and 0.04γNi/cm² (practical).

Effect of Diverse Ions.—Interference was caused by metals that reacted with pyridine and/or rubeanic acid, giving precipitates or coloured solutions (cf. under cobalt). As in the case of cobalt, vanadate, molybdate, tungstate and manganese did not interfere with the nickel estimation. Fe^{III} in very small amounts (less than 10 p.p.m.) could be tolerated as the iron colour showed very little absorption at 530 mμ. The pink colour of nickel was discharged by cyanide.

Thiourea was used to eliminate the interferences due to copper (12 p.p.m.) and silver (20 p.p.m.). But the volume should be made up with water, and the optical density measured within 15 minutes.

Procedure.—Pyridine (15-20 c.c.) was added to a nearly neutral or faintly acidic nickel salt solution, which was free from the interfering ions. In the presence of small amounts of copper and silver, an aqueous solution (3-5 c.c.) of thiourea was added. The solution was then treated with 1 c.c. of 0.1% alcoholic solution of rubeanic acid and the p_H adjusted to 9.8–10.5. The volume was made up with alcohol

(or water, if thiourea added) to 25 c.c., and the optical density measured within 30 minutes against the reagent blank.

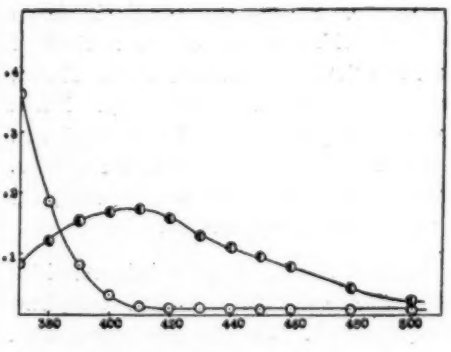
Determination of Palladium

In presence of pyridine, palladium develops an intense orange-yellow colour with rubeanic acid. Palladium has been estimated spectrophotometrically by this means in alcoholic medium at 410 mμ between p_H 4.2 and 7.0. The colour is very stable and follows Beer's law. It can be extracted with *iso*amyl alcohol. The interferences caused by many ions like those of copper, cobalt, nickel, iron, cadmium, etc. can thus be eliminated in presence of disodium salt of etheylenediamine tetra acetic acid, used as a sequestering agent.

Standard palladium solution was prepared by dissolving palladous chloride (Johnson Matthey & Co.) in HCl (conc.) and diluting with distilled water. The palladium content of this solution was determined by dimethylglyoxime. Rubeanic acid solution (0.1%), pyridine and 1% aqueous solution of disodium salt of ethylenediamine tetra-acetic acid were used.

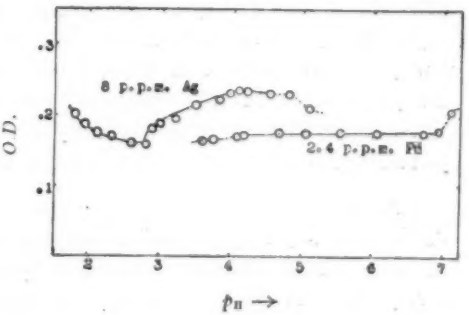
Absorption Curves.—Against a reagent blank, the orange-yellow palladium rubeanate solution showed a maximum optical density at 400-410 mμ, the latter being chosen for all measurements. Fig. 6 shows the variation of optical density with wave-length of the reagent blank and of the palladium complex solution.

FIG. 6



Pd=24 p.p.m. p_H=5.7. Cell=1 cm.

FIG. 7



Concentration of Pyridine and Alcohol.—Pyridide (3-5 c.c.), when added initially, kept the complex in solution without altering its optical density for many hours. Solutions made up with 95% ethyl alcohol remained unchanged for a long time; but with less than 50% alcohol of the total volume, the solutions turned turbid within 1 to 2 hours.

Reagent Concentration.—A 0.1% alcoholic solution (1 c.c.) of rubeanic acid was found to be sufficient for an amount of palladium up to 0.25 mg. in 25 c.c. Higher reagent concentrations had no effect on the colour intensity.

Effect of p_H on the development and stability of colour was studied by measuring the optical density at 410 mμ of solutions, containing 2.4γ Pd, 5 c.c. of pyridine and 1 c.c. of the reagent solution in a total volume of 25 c.c., made up with alcohol. Different p_H values of these solutions were adjusted by the addition of a very dilute acid or ammonia solution. The optimum p_H was found to lie between 4.2 and 7.0, where the maximum colour development was instantaneous (Fig. 7). Above p_H 6.9, the stability of the colour decreased somewhat and the solution became opalescent.

Beer's law was found to hold good for palladium up to 10 p.p.m., above which turbidity set in (Fig. 3).

Stability of the Colour.—The optical density remained unaltered for about 3 days and up to a temperature of 40°.

Sensitivity.—0.013γ Pd/cm² (Sandell) and 0.05γ Pd/cm² (practical).

Effect of Diverse Ions.—Cu^{2+}, Co^{2+}, Ni^{2+}, Pt^{4+}, Au^{3+}, Mo^{6+}, V^{5+}, Ag^{+} etc. interfered. By using versene as the masking agent and then extracting the colour with *iso*amyl alcohol, many of these interferences could be eliminated.

Procedure.—To an acid solution of palladium pyridine (5 c.c.) and the reagent solution (1 c.c.) were added. The p_H of the solution was then adjusted to 4.2–7.0 and the volume made up to 25 c.c. with ethyl alcohol. The optical density of this solution was measured at 410 mμ against the reagent blank.

Estimation of Palladium by Solvent Extraction.—Palladium, though it forms a complex with ethylenediamine tetra-acetic acid (which is one of the methods of determining the metal spectrophotometrically; cf. MacNevin and Kriege, *Anal. Chem.*, 1954, **26**, 1768), reacts with rubeanic acid in its presence in the usual way. But at low p_H values, versene is precipitated in the free state, and in almost neutral solution the palladium rubeanate complex itself is thrown down on making up the volume. These difficulties were overcome by the addition of 3 c.c. of pyridine, adjusting the p_H below 7.0 and by extracting the colour developed with *iso*amyl alcohol.

At p_H 7.0, when sufficient amount of versene is added, copper, cobalt and nickel do not form any deeply coloured complex with rubeanic acid. The versene complexes of these metals are not extractable by *iso*amyl alcohol. Versene also prevents the precipitation of Fe^{III}, cadmium, tin and mercury compounds with pyridine, the versenate complexes of these metals being light coloured or colorless. Molybdate, vanadate and tungstate, which interfere in alcoholic pyridine solution, are also rendered ineffective by this means. Ferrous salt solutions in presence of versene develop a yellow colour with pyridine, which is, however, not extractable with *iso*amyl alcohol. Palladium in presence of a large number of cations can thus be estimated with rubeanic acid with the addition of pyridine and versenate, and by extraction with *iso*amyl alcohol.

The intensity of the coloured extract remained unaltered even after 24 hours at the room temperature. The system was found to obey Beer's law, and gave a sensitivity of 0.013γPd/cm² (Sandell).

Procedure.—To the palladium solution a 1% aqueous disodium versenate solution (1-5 c.c.) was added, followed by 3 c.c. of pyridine. The p_H was adjusted to ~5 to 7 and the solution transferred to a 50 c.c. separating funnel. This was then treated with a 0.1% alcoholic solution of the reagent. The total volume of the mixture should be about 15 to 20 c.c. This was shaken with 5 c.c. of *iso*amyl alcohol and allowed to stand for some time for the separation of layers. The *iso*amyl alcohol layer was collected in a 25 c.c. standard flask. The extraction was repeated twice or thrice with 5 c.c. of *iso*amyl alcohol each time, and the extracts collected in the standard flask. The volume was made up to the mark with *iso*amyl alcohol. A blank was prepared similarly by extracting a solution containing only the reagent, pyridine and sodium versenate. The optical density was measured at 410 mμ against the blank, after filtering the extracts through Whatman No. 1 filter paper to remove suspended water particles. Any precipitation that might occur before extraction should be prevented either by decreasing the volume of the aqueous solution, or by adjusting the p_H, or by the addition of an excess of pyridine or versenate solution. Table I shows the approximate amounts of cations that may be tolerated for 0.05 mg.Pd in a total volume of 25 c.c.

TABLE I

Effect of diverse ions. Pd *rubeanate, solvent extraction*
Pd = 0.05 mg.

Metals	Added as	Na versenate added (1% soln.).	Tolerance limit.	Metals	Added as	Na versenate added (1% soln.)	Tolerance limit.
Co^{II}	Chloride	1 c.c.	30 mg.	Mo^{VI}	Amm. molybdate	2	30 mg.
Cu^{II}	Sulphate	5	3	V^{V}	Na vanadate	4	15
Ni^{II}	Chloride	2	5	W^{VI}	Na tungstate	4	20
Fe^{III}	,,	5	10	Hg^{II}	Chloride	5	10
Fe^{II}	Fe. amm. sulph.	4*	4	Sn^{II}	,,	5**	10
Cr^{III}	Chloride	4	10	Pt^{II}	Acetate	2	15
Cd^{II}	,,	2	10	Zn^{II}	Sulphate	2	15

* Excess pyridine (10 c.c.).
**Saturated versenate soln.

The data recorded in the above table also show the different amounts of versene required to mask the effect of ions concerned. Presence of an excess of versene was always necessary to prevent the precipitation of foreign ions as rubeanates, which might remove some palladium by absorption. In presence of ferrous iron, the palladium rubeanate solution was unstable, turning turbid within a short time. Addition of an excess of pyridine was found to give better results. In this case the volume of the aqueous layer before extraction with *iso*amyl alcohol should be limited to 15 c.c.

Pt^{IV}, Ag^{I} and Au^{III} reacted with rubeanic acid even in the presence of versene, and their complexes were also extractable with *iso*amyl alcohol. They therefore interfere with the estimation of palladium.

Determination of Silver

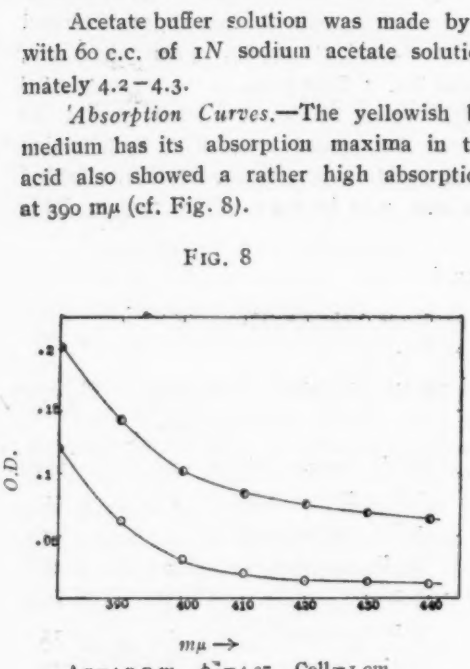
Silver in aqueous medium produces a yellowish brown colour when treated with an alcoholic solution of rubeanic acid. The colour is stable for about one hour. For concentrations of silver above 3γ/c.c., the optical density measured at 390 mμ between p_H 4.0 and 4.6 follows Beer's law. The sensitivity is 0.05γ Ag/cm² (practical).

A solution of silver nitrate (G.R., E. Merck) containing a few drops of nitric acid was used. The silver content was determined as AgCl. A 0.1% rubeanic acid solution in 95% ethyl alcohol was used.

Acetate buffer solution was made by mixing 140 c.c. of 0.2*N* acetic acid (G.R.) with 60 c.c. of 1*N* sodium acetate solution. The p_H of this solution was approximately 4.2–4.3.

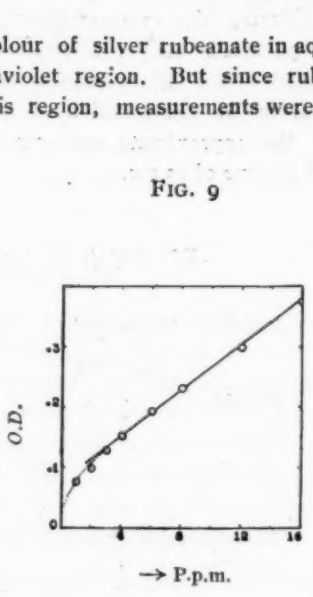
Absorption Curves.—The yellowish brown colour of silver rubeanate in aqueous medium has its absorption maxima in the ultraviolet region. But since rubeanic acid also showed a rather high absorption in this region, measurements were made at 390 mμ (cf. Fig. 8).

FIG. 8



Ag=4 p.p.m. p_H=4.27. Cell=1 cm.

FIG. 9



Reagent Concentration.—Maximum colour intensity was obtained with 1 c.c. of 0.1% alcoholic solution of the reagent, when the silver content was less than 16γ Ag/c.c. Excess of the reagent had no effect on the colour intensity.

Effect of p_H.—The optimum p_H range was found to lie between 4.0 and 4.6 (Fig. 7), where the maximum intensity was attained within a few minutes after the addition of the reagent. The solution gradually turned opalescent at or above p_H 4.6.

Beer's Law.—The system was found to obey Beer's law between 3 and 20γ Ag/per c.c. (Fig. 9).

Stability of the Colour.—The optical density of a solution containing 4γ Ag/c.c. remained constant for about 1½ hours, beyond which turbidity appeared. The optical density and the stability of the colour remained unchanged up to 35°.

Sensitivity.—0.05γ Ag/cm³ (practical).

Effect of Diverse Ions.—The determination of silver by rubeanic acid is possible only in the absence of metals which either give precipitate or coloration with rubeanic acid (cf. under cobalt). These metals even when present in very small amounts interfere with the estimation of silver.

Procedure.—The p_H of the sample solution, containing only silver, was adjusted to 4.0-4.6. This can also be achieved by the addition of 10 c.c. of sodium acetate-acetic acid buffer, added after the reagent solution. A 0.1% alcoholic solution of rubeanic acid (1 c.c.) was then added to the above solution and the volume made up to 25 c.c. with distilled water. The optical density was measured at 390 mμ within 30 minutes, against a suitable blank.

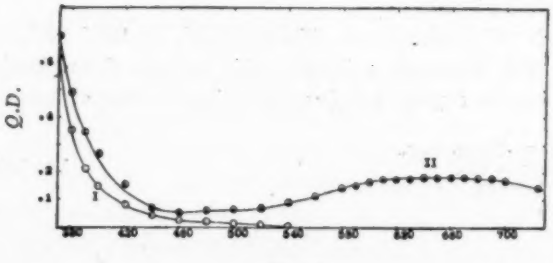
Determination of Ruthenium.

The spectrophotometric determination of ruthenium by rubeanic acid has been reported by Ayres and Young (*loc. cit.*). They observed that a high concentration of hydrochloric acid was required to develop the colour and that a large amount of ethyl alcohol was desirable to prevent the precipitation of the complex. It was further noticed by them that at room temperature the colour developed very slowly, while at elevated temperatures the reaction was more rapid.

A critical examination of the procedure was deemed necessary as some difficulties were experienced, when substituted rubeanic acids were used for the determination of ruthenium. This had led to the following modification of Ayres and Young's method.

Ruthenium trichloride (Johnson Matthey & Co) was dissolved in HCl (conc.) and the volume made up in a standard flask. The solution was standardised according to the method of Gilchrist aud Wichers (precipitating as the hydroxide and weighing as the metal; *J. Amer. Chem. Soc.*, 1935, **57**, 2565). 0.2% Rubeanic acid in acetic acid was used as the reagent solution.

FIG. 10



Ru = 2 p.p.m. Reagent = 1 c.c. Cell = 1 c.c.

Absorption Curves.—The greenish blue colour of ruthenium rubeanate has its absorption maxima in the region 640-670 mμ (cf. Fig. 10). The colour was developed by adding 1 c.c. of rubeanic acid solution to ruthenium solution (2 p.p.m.), containing 5 c.c. of a mixture (1 : 1 by vol.) of ethyl alcohol (95%) and 12*N*-HCl and warming on a water-bath for about 30 minutes. The volume was then made up to 25 c.c. with EtOH-HCl (6*N*) mixture (1 : 1 by vol.).

Reagent Concentration.—The minimum amount of the reagent required by 0.1 mg. Ru to develop the maximum colour intensity was found to be 1 c.c. of 0.2% rubeanic acid solution in acetic acid. Ayres and Young (*loc. cit.*) added 15 c.c. of the same in 100 c.c. final volume. But addition of an excess of the reagent is disadvantageous, as the region of absorption maxima is less sharp, probably due to the change in the tinge of colour (bluish green).

Effect of Acid Concentration.—The amount of acid-alcohol mixture (1 : 1 by vol. of 12*N*-HCl and 95% EtOH), added before developing the colour, was varied from 1 c.c. to 10 c.c., and the effect on optical density studied. It was found that variation in acid concentration did not affect the colour intensity. The ruthenium solution used for these studies was already acidic with HCl (about 1*N*). Addition of a large excess of acid, as prescribed by Ayres and Young, is therefore, unnecessary.

Beer's Law Curve.—The colour system closely followed Beer's law for ruthenium concentrations up to 4 p.p.m. (cf. Fig. 3). The previous workers noticed that the concentration limit to which Beer's law was valid, lay below 2·2 p.p.m., using 15 c.c. of the reagent solution for 100 c.c. final volume.

Sensitivity.—0.011γ Ru/cm² (Saudell) and 4.04γ Ru/cm² (practical).

Effect of Diverse Ions.—Tolerance limits of foreign ions, especially of the platinum metals, have been determined by Ayres and Young (*loc. cit.*). It was observrd that osmium interfered seriously, while platinum, palladium, rhodium and iridium were permissible in very small amounts.

Procedure.—To the ruthenium solution which gave a final concentration of not more than 4 p.p.m., 2-5 c.c. of a mixture (1 : 1 vol.) of 12*N*-HCl and 95% ethyl alcohol and 1 c.c. of rubeanic acid solution (0.2%) were added. The mixture was warmed on a water-bath for about 30 minutes. The volume was then made up to 25 c.c. with 95% EtOH-6*N*-HCl mixture (1 : 1 by vol.), and the optical density measured at 670 mμ against a suitable blank.

The use of N : N′-disubstituted (like dimethyl, diethyl, dibenzyl, di-*iso*amyl, di-β-hydroxyethyl and diphenyl) rubeanic acids for the determination of the above mentioned metals, besides copper, will form the subject matter of future communications.

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FORMATION OF ALUMINIUM o-CRESOTATE CHELATE: POTENTIOMETRIC AND CONDUCTOMETRIC STUDIES

By S. C. Tripathi* and Satya Prakash

Increase in H^+-concentration of monosodium *o*-cresotate has been observed on the addition of aluminium chloride solution The increase in H^+- concentration may be ascribed to the displacement of hydroxyl hydrogen in the complex formation. In the potentiometric and conductometric titration curves of 1 : 1, 1 : 2, 1 : 3 and 1 : 4 mixtures of aluminium chloride and monosodium *o*-cresotate, the inflections and breaks at one equivalent of alkali indicate the formation of a complex containing aluminium and *o*-cresotate in 1 : 1 ratio. The second inflection at three equivalents of alkali shows the precipitation of aluminium hydroxide.

Aluminium forms complexes with malic (Delsal, *J. chim. phys.*, 1938, **35**, 350), tartaric (Spacu and Popper, *Kolloid Z.*, 1943, **103**, 19) and salicylic acids (Burrows and Wark, *J. Chem. Soc.*, 1928, 222) and with 2 : 3-dihydroxynaphthalene (Weinland and Seuffert, *Arch. Pharm.*, 1928, **266**, 455). Moser *et al.* (*Monatsh.*, 1922, **43**, 678) have shown that in presence of sulphosalicylic acid, aluminium is not precipitated as hydroxide. Aluminium salts of sulphosalicylic, sulphobenzoic and sulphohydroxynaphthoic acids have been prepared by Dominikiewicz (*Arch. Chem. Pharm.*, 1934, **1**, 93). Salicylate complexes have been investigated in detail by Babko *et al.* (*J. Gen. Chem. U.S.S.R.*, 1948, **18**, 1617). In weakly acidic solutions, a complex $(Al\ Sal)^+$ is formed. With rise in p_H and the corresponding increase in the concentration of salicylate ions, a second and a third stage of the complex formation take place, consistent with the formation of $(Al\ Sal_2)^-$ and $(Al\ Sal_3)^{3-}$ successively. Illari (*Anal. Chim. Appl.*, 1952, **42**, 32) obtained crystals of aluminium salicylate by refluxing aluminium nitrate and salicylic acid. Spectrophotometric study of the complex formation between aluminium and sulphosalicylic acid was carried out by Anderson and Lasater (*J. Amer. Chem. Soc.*, 1952, **74**, 1429) and the formation of 1 : 1 complex up to p_H 5.0 was confirmed.

Singh (D. Phil. thesis, Allahabad Univ., 1956) has investigated 1 : 1 and 1 : 2 complexes of aluminium with sulphosalicylic and chloromercuri-sulphosalicylic acids by potentiometric and conductometric methods.

Experimental

Standard solutions of aluminium chloride were made by dissolving Baker's analysed sample of $AlCl_3$, $6H_2O$ in water and the aluminium content was estimated gravimetrically as $Al(C_9H_6ON)_3$ with 8-hydroxyquinoline (oxine) (Vogel, "Text-book of Quantitative Inorganic Analysis", 1951, p. 372).

Monosodium salt of *o*-cresotic acid was prepared by the addition of an equivalent amount of an E. Merck-A.R. sample of sodium bicarbonate in a B.D.H.-L.R. sample of

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o-cresotic acid. The mother-liquor was evaporated to dryness on a water-bath. The crude sample of monosodium salt of *o*-cresotic acid was crystallised in absolute alcohol in white shining crystals and dried in a desiccator. Carbon, hydrogen and oxygen contents were determined by combustion. Standard solutions of monosodium *o*-cresotate were prepared by direct weighing of the prepared sample.

All the measurements were made at a constant temperature of 32° ± 0.1° ; p_H was measured with a Leeds Northrups A.C.-operated p_H-meter using glass and saturated calomel electrodes. The instrument was standardised with a standard buffer solution.

Electrical conductivity was measured by a Leeds Northrups Kohlrausch slide wire bridge with an A. C. -operated audiofrequency oscillator in the circuit. The null point was detected by the headphone supplied by the same manufacturers.

Complex-forming Systems.—To study the complex formation of aluminium with monosodium *o*-cresotate, monovariant method was used. To constant volumes of aluminium chloride varying amounts of monosodium o-cresotate were added. Thus, a number of sets of mixtures containing aluminium chloride and monosodium o-cresotate in the ratios of 1 : 1, 1 : 2, 1 : 3 and 1 : 4 were prepared. To these mixtures varying amounts of standard solutions of caustic soda were added. The total volume of the mixtures was kept constant in each case. The sets were left for about 24 hours to attain the equilibrium. p_H and specific conductivity of the mixtures were measured at a constant temperature. For comparison, aluminium chloride and monosodium *o*-cresotate were titrated separately with alkali by potentiometric and conductometric methods under similar conditions.

Discussion

In the graphs, the number of equivalents of alkali is represented by abscissa while physical properties, viz., p_H and specific conductivity, by ordinate.

FIG. 1

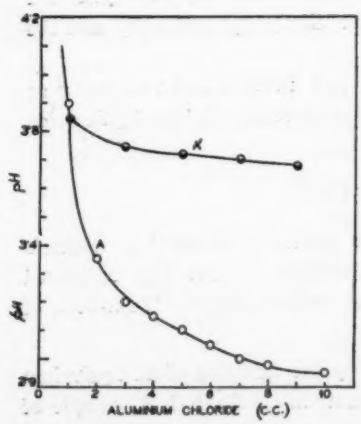
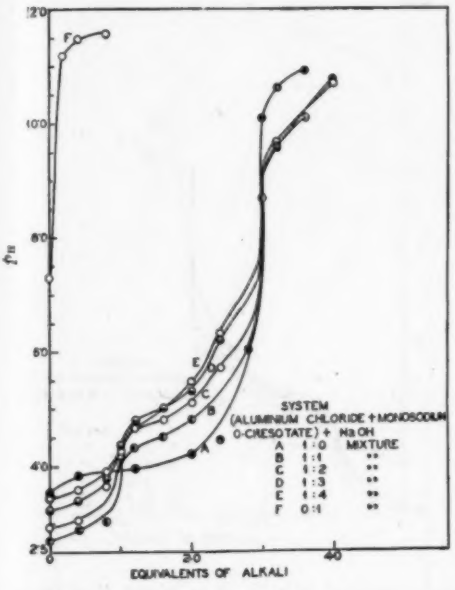


Fig. 1 represents the changes in hydrogen-ion concentration in monosodium *o*-cresotate (0.05 *M*) solution by the addition of varying amounts of aluminium chloride (0.05 *M*). The curve A shows that p_H of monosodium *o*-cresotate (6.80) decreases by the addition of aluminium chloride. No major change is brought about in the p_H of the mixture after 3.1, when about one equivalent of aluminium chloride is added. Curve A′ represents the p_H of aluminium chloride only at similar concentrations. As the curve A for the mixture lies below A′, it is evident that there is an increase in hydrogen-ion concentration in the system, which is only possible by the displacement of hydroxyl hydrogen of *o*-cresotate by aluminium. This shows that aluminium forms a complex with *o*-cresotate ; the reaction may be represented as :

$$C_7H_6(OH)—COONa + Al^{3+} \rightarrow [(C_7H_6.O—COO)Al]^+ + H^+ + Na^+ \quad \ldots (i)$$

Fig. 2 shows the variation of hydrogen-ion concentration with the progressive addition of alkali to the systems: (*i*) aluminium chloride (0.10 *M*) (curve A) and mixtures of aluminium chloride (0.10 *M*) and monosodium *o* cresotate (0.10 *M*) in the ratios of (*ii*) 1 : 1 (curve B), (*iii*) 1 : 2 (curve C), (*iv*) 1 : 3 (curve D) and (*v*) 1 : 4 (curve E), while the curve F shows the reaction of alkali on monosodium *o*-cresotate itself.

FIG. 2



In curve A (Fig. 2), the precipitation of aluminium hydroxide started at about p_H 6.05 and was complete when three equivalents of alkali were added. At about p_H 10.5, when addition of four equivalents of alkali was complete, the precipitate of aluminium hydroxide dissolved, forming aluminate. The reaction can be represented by the following equations:

$$AlCl_3 + 3\ NaOH \rightarrow Al(OH)_3 + 3\ NaCl \quad \ldots (ii)$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O \quad \ldots (iii)$$

From curve F (Fig. 2), it is clearly indicated that no liberation of hydroxyl hydrogen of monosodium *o*-cresotate takes place by alkali, and by the addition of only a little alkali there is a steep rise in p_H (7.30 to 11.20), showing no free hydrogen ion present in the system to be titrated by alkali.

When varying amounts of alkali were added in the mixtures (1 : 1-1 : 4) of 0.10 *M* aluminium chloride and 0.10 *M* monosodium *o*-cresotate, a small amount of a white precipitate appeared in the systems, but when the sets were left to attain the equilibrium, the precipitate formed was seen to dissolve up to about p_H 5.0, and above this p_H (5.0) a gelatinous white precipitate of aluminium hydroxide persisted (curves B, C, D, E, Fig. 2). The precipitation of aluminium hydroxide was completed by the addition of three equivalents of alkali, and the gelatinous white precipitate of aluminium hydroxide again dissolved after the addition of four equivalents of alkali, forming aluminate (equations *ii* and *iii*).

FIG. 3

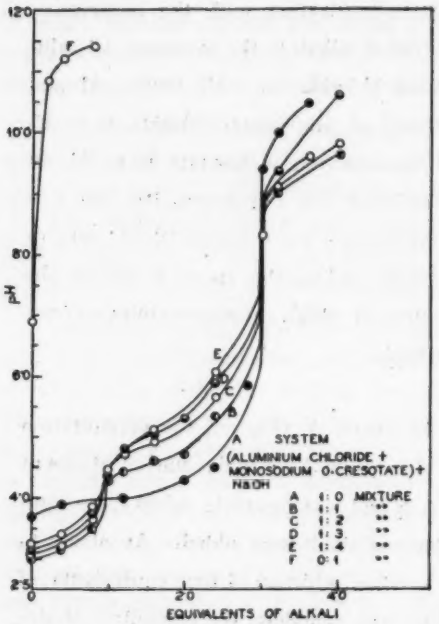
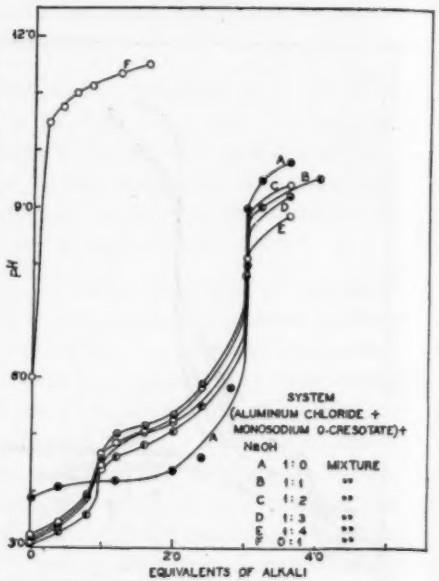


FIG. 4



When the p_H is plotted against the equivalents of alkali, it is clear that there is one inflection in the curves B, C, D, E (Fig. 2) at one equivalent of alkali, showing the complete precipitation of aluminium hydroxide. The occurrence of first inflection can be explained by assuming that at about p_H 4.25, a complex is completely formed containing aluminium and *o*-cresotate in 1 : 1 ratio. It can also be inferred from the curves that in the formation of the complex, the hydroxyl hydrogen of *o*-cresotate is displaced by aluminium and oxygen atoms of hydroxyl and carboxyl groups share in the complex formation. The reaction can be represented by equation (*i*).

The complex started breaking at about p_H 5.0, resulting in the precipitation of aluminium hydroxide, which was complete at about p_H 8.0.

Figs. 3 and 4 represent the results of p_H measurements in similar experiments, as in Fig. 2, with two lower concentrations (0.05 *M* and 0.025 *M*) of the reactants. The curves A, B, C, D, E and F of Figs. 3 and 4 are of exactly similar nature as curves A, B, C, D, E and F of Fig. 2 which provide sufficient evidence for the formation of complex of aluminium with *o*-cresotate, containing aluminium and *o*-cresotate in 1 : 1 ratio, in acidic medium.

Similar observations were made with the specific conductivity study (Fig. 5). The curve A (Fig. 5) shows the conductometric titration of aluminium chloride (0.10 *M*) with caustic soda. From the examination of the curve A (Fig. 5), it is seen that there is a definite break in the curves at about three equivalents of alkali, which shows

the complete precipitation of aluminium hydroxide. By the addition of four equivalents of alkali, the gelatinous precipitate of aluminium hydroxide dissolved completely, forming aluminate. The reaction can be represented by equations (*ii*) and (*iii*).

FIG. 5

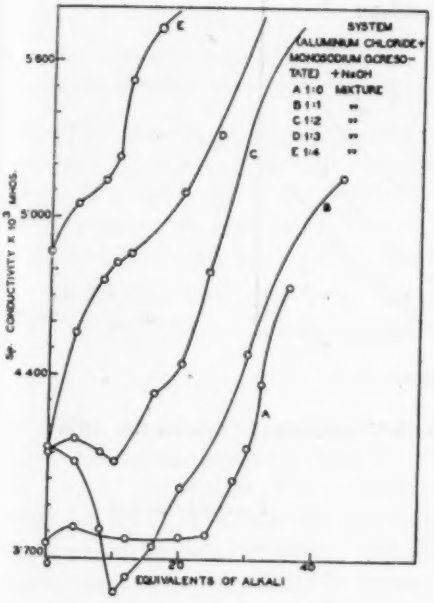
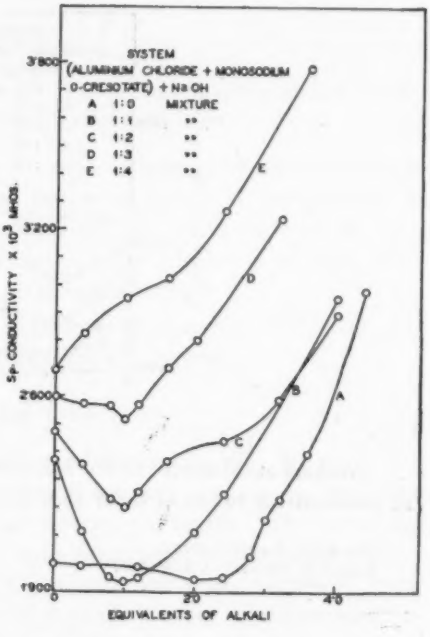


FIG. 6



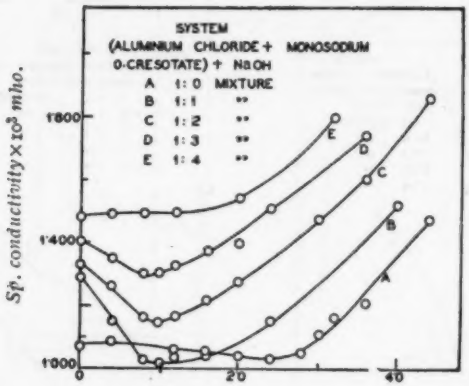
The curves B, C, D and E (Fig. 5) represent the conductometric titration of (1 : 1, 1 : 2, 1 : 3 and 1 : 4) mixtures of aluminium chloride (0.1 *M*) and monosodium *o*-cresotate (0.10 *M*) respectively by alkali. All the curves show only one break at one equivalent of alkali. This shows the formation of only one complex of aluminium and *o*-cresotate containing the two reactants in 1 : 1 ratio. The reaction may be represented by equation (*i*).

In Figs. 6 and 7, the results of similar experiments, as in Fig. 5, with two lower concentrations (0.05 *M* and 0.025 *M*) of the reactants obtained by specific conductivity study are plotted graphically. All the curves, A, B, C, D and E of Figs. 6 and 7, give the same conclusion as shown by the curves of Fig. 5. It also shows the formation of only one complex containing aluminium and *o*-cresotate in 1 : 1 ratio.

From the above observations of p_H and specific conductivity measurements (Figs. 1-7), it has become quite clear that aluminium forms only one complex with monosodium *o*-cresotate in 1 : 1 ratio. In case of salicylic acid, Babko *et al.* (*loc. cit.*) have shown the formation of three complexes with aluminium, but in the case of *o*-cresotate there is indication of formation of only one complex. They have pointed

out that in weakly acidic solutions, aluminium forms 1 : 1 complex with salicylic acid. With rise in p_H and concentration of salicylic acid, other complexes of 1 : 2 and 1 : 3 ratios, with respect to aluminium and salicylate, are formed.

FIG 7



Authors are thankful to the Scientific Research Committee of U.P. for the award of an assistantship to one of them (S.C.T.).

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ION-ACTIVITY MEASUREMENT WITH RESIN-MEMBRANE ELECTRODES: MEASUREMENT OF ZINC, CADMIUM AND MANGANESE ION ACTIVITY IN ELECTROLYTIC SOLUTIONS

By A. S. Basu

Measurement of ion-activity of bivalent metals like Zn^{2+}, Cd^{2+} and Mn^{2+} has been made with resin-membrane electrodes, providing values agreeing closely with the theoretical values.

The resin membrane electrodes have been successfully used by Wyllie and Patnode (*J. Phys. Chem.*, 1950, **54**, 204) and by Sinha for the measurement of ion-activities of Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+} and Cu^{2+} (this *Journal*, 1954, **31**, 572; 1955, **32**, 399). The measurements along this line have been extended to other bivalent ions like Zn^{2+}, Cd^{2+} and Mn^{2+}, and the results are recorded in this communication.

Mitra and Chatterjee (*ibid.*, 1953, **32**, 751) satisfactorily measured Zn^{2+}, Mn^{2+} and Co^{2+} ion-activities in electrolytic solution with clay membrane electrodes.

Experimental

The resin membranes were prepared according to Sinha (*ibid.*, 1953, **30**, 529) using three commercial cationites, Ionac-C-200, Amberlite-IR-100 and IR-120, by moulding at 120-30° at 4000 lbs./P.S.i. pressure with polystyrene as binder. The electrodes were prepared by fixing the membranes, cut into small sizes, to one end of a pyrex tubing with 'Durofix' adhesive. The asymmetry potential was tested as usual. The membranes showing negligible or zero asymmetry potential were then interposed between solutions of known ion-activities. Owing to their stability in solution relative to chlorides, sulphates of zinc, cadmium and manganese were preferred. Such standard solutions were prepared as could make the ratio of ion-activities of any suitable pair equal to 3 : 1; the activity coefficients were calculated in very dilute as well as in very concentrated solutions by graphical extrapolation (Lewis and Randall, "Thermodynamics"). Mn^{2+}-ion activities were calculated assuming the activity coefficients to be the same as that of Zn^{2+} and Cd^{2+} (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions"). The E.M.F. of the following cell:

Hg, Hg_2Cl_2	Satd. KCl	Solution a_1	Resin membrane electrode	Solution a_2	Satd. KCl	Hg_2Cl_2, Hg

was measured by means of the L & N K_2-type potentiometer in combination with a Hartmann and Braun galvanometer having a current density 10^{-10} amps./mm/m. The readings, accurate within ± 0.1 mv, were taken by interchanging the solutions inside and outside the pyrex tubing to check as well as eliminate asymmetry potential, if any.

The equilibrium was attained fairly quickly in concentrated solutions, but in dilute solutions, a longer time, often about 24 hours, was required. The reproducibility of

measurement was checked by repeated changes of solutions. The electrical resistance of the membranes was found to be within one megohm. For comparison, the theoretical E.M.F.s were calculated by means of the simple Nernst equation,

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_2},$$

which has been proved to hold good in the case of such membrane electrodes as those used here.

TABLE I

Theoretical value = 14.1.

Ratio of activities.		E. M. F.							
Inside.	Outside.	Zn-ion.			Cd-ion.			Mn-ion.	
a_1.	a_2.	Ionac-C2co.	IRA-100.	IR-120.	Ionac-C200.	IRA-100.	IR-120.	Ionac-C200.	IRA-100.
0.0081	0.0027	14.0	13.8	13.7	11.9	13.9	11.6	13.6	10.0
		14.2*	13.9*	13.9*	11.5*	13.5*	11.2*	13.0*	10.5*
0.0027	0.0009	14.0	14.0	13.8	13.5	15.0	15.0	13.5	10.5
		13.8*	14.5*	14.5*	13.0*	14.0*	14.0*	14.5*	11.5*
0.0009	0.0003	14.2	13.8	13.0	14.9	15.0	12.5	11.5	11.0
		14.0*	13.0*	12.8*	14.5*	15.5*	13.0*	12.5*	12.5*
0.0003	0.0001	14.0	15.0	16.0	14.6	12.6	11.0	13.5	10.5
		13.5*	15.5*	15.0*	14.0*	11.5*	11.5*	13.0*	10.0*

The first sets of figures correspond to the arrangements of solutions as shown in columns 1 and 2, whereas the second sets, marked with an asterisk, have been obtained by interchanging the solutions inside and outside the membrane electrodes. The mean of the sets is compared with the theoretical values.

Accurate data on the activity coefficients of the salt solutions are not available. Moreover, the Lewis and Randall assumption for the calculation of the activities of ion is very approximate. However, a comparison of the theoretical E.M.F.s with the observed values shows clearly that in spite of the likely discrepancies, mentioned above, the agreement is fairly good. The agreement is more satisfactory within the range (a=0.0081 to a=0.0001) of solutions. Of the three resins, Ionac-C-200 gives the best performance.

Thanks are due to Dr. S. K. Mukherjee, University College of Science and Technology, for his valuable suggestions and guidance, and to Dr. P. C. Rakshit, Head of the Department of Chemistry, Presidency College, for his continued interest and for giving laboratory facilities, and also to the Ministry of Education, Govt. of India for the grant of a senior research scholarship.

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SHORT NOTES

VOLUMETRIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF SILVER IN PRESENCE OF LARGE AMOUNTS OF COPPER AND NICKEL

By K. C. Seal

The titration of silver by Volhard's method has some limitations if copper also is present. Determination of silver in ores and alloys by starch-iodine method (Pisani, *Ann. Min.*, 1856, 83 ; Field, *Chem. News*, 1860, **2**, 17) is not satisfactory when the percentage of copper is very high as it would be difficult to weaken the colour of the copper and nickel even by large dilution.

In the present work the reaction of silver ion with iodine in potassium iodide solution has been studied under different p_H and it has been found that the determination of silver by titrating with iodine-iodide solution, using starch as an internal indicator, can be done in the presence of an excess of sodium acetate or sodium bicarbonate. In sodium acetate buffer medium, the end-point is more sharp. Hence, this medium has been chosen for the present determination. Here, both iodine and iodide enter into the reaction whereas in ordinary iodimetry, the concentration of iodine alone counts. Hence, iodine-iodide solution is standardised against a known silver nitrate solution. The presence of copper and nickel will not interfere with the estimation.

Silver salts react with iodine with the formation of unstable hypoiodous acid which is more stable in neutral or acidic medium :

$$Ag^+ + I_2 + H_2O = AgI + HIO + H^+.$$

But in sodium acetate buffer medium, the decomposition of hypoiodous acid to iodic acid is practically complete and the regenerated HI further reacts with the silver salts :

$$\begin{aligned} 3Ag^+ + 3I_2 + 3H_2O &= 3HIO + 3AgI + 3H^+ \\ 3HIO &= HIO_3 + 2HI \\ 2Ag^+ + 2HI &= 2AgI + 2H^+ \\ \hline 5Ag^+ + 3I_2 + 3H_2O &= 5AgI + HIO_3 + 5H^+ \end{aligned}$$

This reaction can be substantiated by determining the amount of KI and free iodine present per c.c. of iodine-iodide solution. The reaction of silver salts with KI is simple :

$$Ag^+ + KI = AgI + K^+$$

Procedure.—Pure KI (10.0 g.) was dissolved in distilled water (15-20 c.c.) ; pure iodine (A.R., 6.3 g.) was carefully introduced into the KI solution and stirred in the

cold till the iodine completely dissolved. Immediately, the solution was transferred to a glass-stoppered 2-litre flask and the volume made up to the mark with distilled water.

To a neutral $N/50$-$AgNO_3$ solution (10 or 20 c.c.), taken in a 250 c.c. conical flask, a 20% sodium acetate (extra pure) solution (25 c.c.) was added and diluted to 100 c.c. with distilled water. A freshly prepared 1% starch solution (2-3 c.c.) was added and then it was titrated slowly with iodine-iodide solution from a burette to the first definite starch-iodine end-point. A blank test was carried out taking 100 c.c. of distilled water containing 5.0 g. of sodium acetate. The volume of iodine-iodide solution required in the blank titration was deducted from the volume required in the original titration. The silver value of 1 c.c. of iodine-iodide solution was thus determined. It is important to carry out this standardisation for each set of experiments.

Determination of Silver.—The material (2.5 g.) was dissolved in HNO_3 (d 1.2) and then fumed with 10 c.c. of H_2SO_4 (conc.) cautiously over a sand-bath. Most of the acid was removed by fuming. The residue was dissolved in distilled water and transferred to a 250 c.c. measuring flask, filtering, if necessary, and the volume was made up to the mark. An aliquot volume of the solution was taken in a 250 c.c. flask, neutralised by $NaHCO_3$ solution (conc.), added dropwise from a burette, and then titrated as usual with the standard iodine-iodide solution after adding sodium acetate. The results are shown in Table I.

TABLE I

No.	% Cu in mixture.	% Ni in mixture.	Ag (calc).	Ag (found).	% Error.
1.	99.20	Nil	0.00405 g.	0.00403 g.	0 49
2.	98 93	Nil	0.00540	0 00542	0.37
3.	97.89	Nil	0.01080	0.01091	1.01
4.	95.76	Nil	0.02214	0.02236	0.99
5.	92·05	Nil	0.02160	0.02147	0.60
6.	88.52	Nil	0.03240	0.03266	0.80
7.	85.26	Nil	0.04320	0.04298	0.51
8.	82.23	Nil	0.05400	0.05400	0.00
9.	54.25	43.40	0.01080	0.01089	0.83
10.	52.31	43.24	0.02160	0.02151	0 41
11.	63.58	24 43	0.04320	0.04316	0.09
12.	43.10	45 26	0.05400	0.05378	0.41

The author's thanks are due to the Director General, Supplies and Disposals and the Director, Government Test House, for their kind permission to carry out the work in the Government Test House Chemical Laboratories in spare time.

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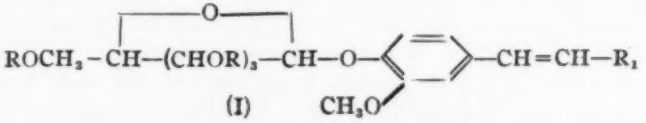
ATTEMPTS ON THE SYNTHESIS OF CONIFERIN

By Durgeshwari Prasad and D. N. Chaudhury

The glucoside, coniferin (I: R=H ; R_1=CH_2OH), was first isolated from the sap of the cambium of Coniferae by Tiemann and Harmann (*Ber.*, 1874, **7**, 611) who showed that it was a β-*d*-glucoside of coniferyl alcohol.



(I)

Pauly and Feurstein (*Ber.*, 1927, **60**, 1031) claimed to have synthesised the glucoside by a biochemical method, although they failed to synthesise it by a purely chemical method. Attempts have therefore been made to synthesise coniferin by steps involving standard chemical reactions.

Thus, methyl ferulate, prepared by an improved method, was condensed with *O*-tetra-acetyl-α-*d*-glucosidyl bromide in aqueous-alkali-acetone when the hitherto unreported methyl-3-methoxy-4-tetra-acetyl-β-*d*-glucosidoxy-cinnamate (I: R = Ac ; R_1= $-CO_2Me$) was obtained in good yield. Attempts to reduce the ester group of the foregoing compound with lithium-aluminium hydride, with a view to obtaining coniferin, however, unaccountably failed although varying conditions for reduction were employed ; the starting material was invariably recovered unchanged in each case.

The following improved procedure was adopted in which the conversion of acetoferuloyl chloride to the corresponding ester proceeded with simultaneous deacetylation to yield methyl ferulate.

(*a*). A mixture of 4-acetylferuloyl chloride (9.6 g.) (Fosdick and Starke, *J. Amer. Chem. Soc.*, 1940, **62**, 3353), methyl alcohol (40 c.c.) and pyridine (9 drops) was refluxed for 3 hours ; excess methyl alcohol was distilled off and water added when a brown oil separated which thickened on cooling in a refrigerator. The water was decanted and the thick oil was taken up in ether ; the ethereal solution was washed with water, dried ($MgSO_4$) and the ether evaporated. The gummy residue on distillation under reduced pressure (2.9 mm/180-90°, bath temp.) afforded a yellow viscous oil which, on keeping in the refrigerator for a week, deposited at places rosettes of needles ; when rubbed with a glass rod and left in the refrigerator overnight, methyl ferulate solidified to a thick paste of crystalline needles, which were crystallised from methyl alcohol, m.p. 65°, yield 4.8 g.

(*b*). Pyridine (3 drops) was added with shaking to acetoferuloyl chloride (1.0 g.), suspended in methyl alcohol (5 c.c.), when the reaction mixture became warm and part of the acid chloride went into solution. After a few minutes, the whole mixture solidified to a thick paste of crystals. An additional quantity of methyl alcohol (5 c.c.)

and pyridine (3 drops) were added and warmed gently for 2-3 minutes until a clear solution was obtained. On keeping, the solution deposited crystalline methyl acetoferulate which on recrystallisation from methyl alcohol yielded the pure specimen (0.8 g), m.p. 122°. Deacetylation was effected by boiling with MeOH-HCl (conc.) (4 drops) for ten minutes and the oil, obtained after evaporating the excess methyl alcohol, deposited methyl ferulate, when nucleated with the specimen obtained in expt. (*a*). Crystallised from methyl alcohol, it melted at 65°.

Acetylation of methyl ferulate with acetic anhydride-pyridine on a water-bath for one hour yielded methyl acetoferulate, m.p. and mixed m.p. 123°.

Methyl 3-Methoxy-4-tetra-acetyl-β-d-glucosidoxy-cinnamate (I : R = Ac ; $R_1 = CO_2Me$). —*O*-Tetra-acetyl-α-*d*-glucosidyl bromide (6.3 g.) in acetone (50 c.c.) was added to methyl ferulate (4.5 g.), dissolved in aqueous caustic soda (0.9 g in 27 c.c. water) and the homogeneous red solution was set aside for 16 hours at the room temperature. It was then extracted with benzene (30 c.c. × 3), the combined extract washed with water (60 c.c.) containing NaOH (2 drops ; 2*N*) and then with water (60 c.c. × 3), dried ($CaCl_2$), filtered and the benzene removed under reduced pressure. The viscous oily residue was dissolved in the minimum quantity of methyl alcohol by warming ; on keeping in the refrigerator, the solution deposited white shining needles which after three recrystallisations from methyl alcohol yielded the pure *glucoside*, m.p. 140°, yield 4.25 g. (Found : C, 55.8 ; H, 5.3. $C_{25}H_{30}O_{13}$ requires C, 55.76 ; H, 5.57%). $[\alpha]_D^{32.5} = -31°.08$ (*c* in $CHCl_3$, 0.0458).

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Received January 31, 1958.

INDIAN CHEMICAL SOCIETY

BASUDEV BANERJEE MEDAL & PRIZE 1959

Appplications are invited for the Basudev Banerjee Medal and cash Prize of Rs. 400/- to be awarded on the merit of research contribution in Organic Chemistry (including Biochemistry).

Applications with **4 copies of reprints or typescripts** of the papers should reach the undersigned on or before 15th October, 1958. The conditions of the award are noted below.

M. M. Chakrabarty.
Hony. Secretary

BASUDEV BANERJEE MEDAL AND PRIZE 1959.

(Conditions of the Award)

1. That the value of the Prize should be about Rs. 400/- in cash and that of the Medal about Rs. 100/-.

2. That the Medal and the Prize should be open for competition amongst all persons who have been admitted to a degree in science of any Indian University. That the age of the person competing for the award should not be more than **42 on the 30th March** of the year of the award.

3. That the Medal and the Prize should be awarded for the best piece of independent and/or joint research work in **organic chemistry** (including **biochemistry)** as judged by a committee of experts appointed by the Council of the Indian Chemical Society. Only such work which has been published in any scientific journal in the course of the preceding five years (i.e. after 30th March, 1954) may be submitted for the competition.

In case of joint work, only the author under whose guidance the work was carried out is entitled to compete.

4. That the announcement of the result of the competition should be made at the Society's meeting held at the time of the annual sessions of the Indian Science Congress Association and made public through suitable news organs.

5. That the Medal and the Prize should be presented at a special meeting of the Society to be expressly called for this purpose and to be held at a suitable place as decided by the Council of Indian Chemical Society, on the 30th March, the birthday of the late Dr. Banerjee.

6. That the recipient of the Prize and the Medal should be required to deliver, at the time of the award, a lecture to be called the "Basudev Banerjee Memorial Lecture", the subject matter of which will be based on the work that has been submitted for the competition. The **manuscript of the lecture should be submitted one month before the presentation of the award** and will be published in any of the organs of the Indian Chemical Society.

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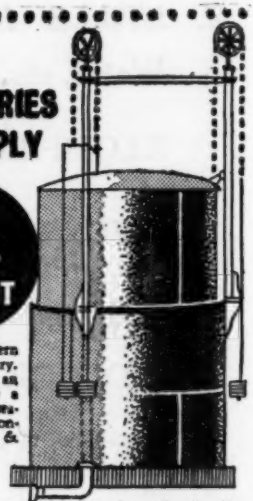

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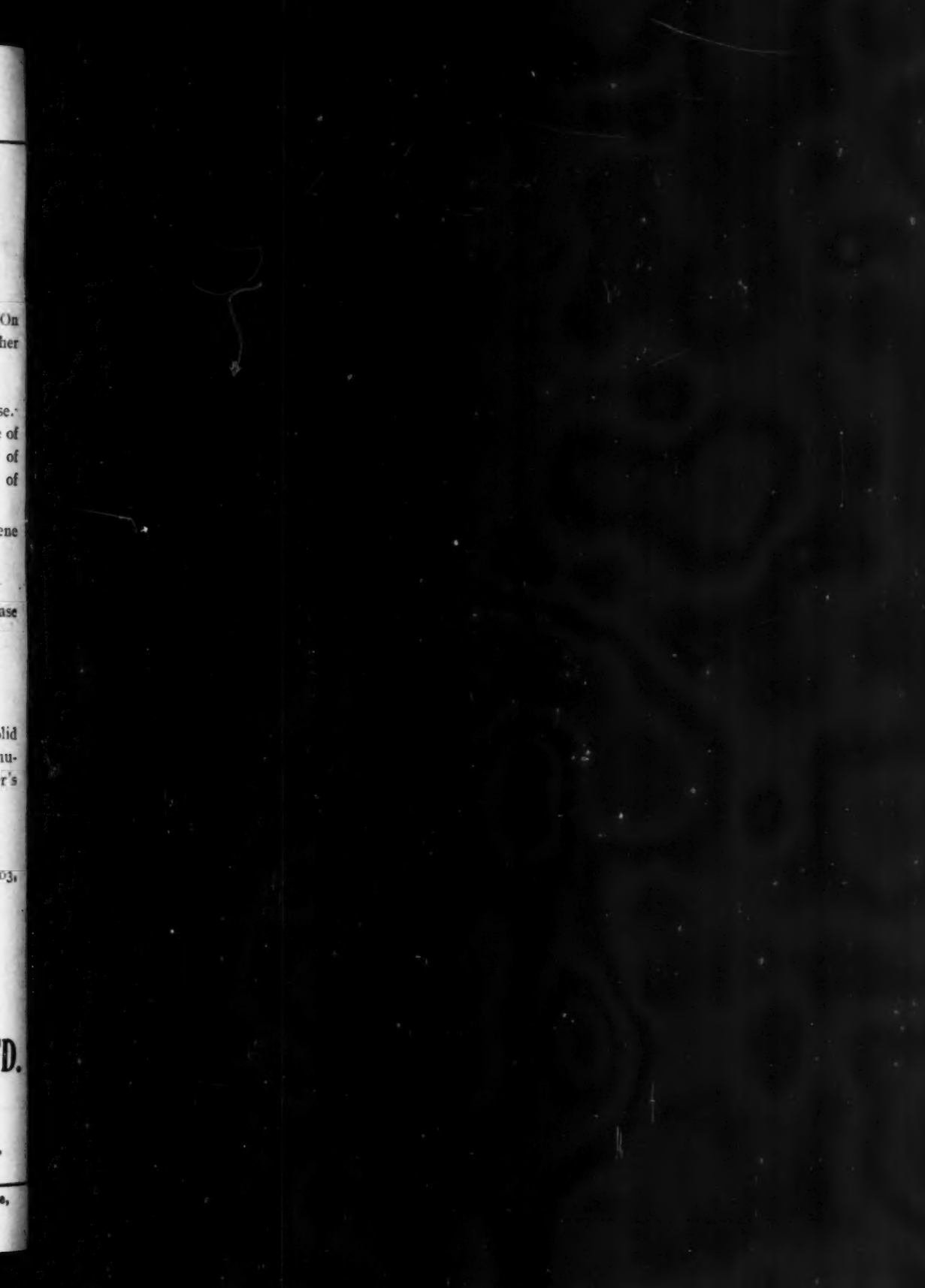
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